

BNL-MOX-2009-001

DRAFT

Risk Assessment of Red Oil Excursions in the MOX Facility

Date Published: May 2009

V. Mubayi, M. A. Azarm*, M. Yue, W. Mukaddam**, G. Goode**, R.A. Bari, and F. Gonzalez***

Brookhaven National Laboratory
Upton, NY 11973-5000

*ISL, Inc.

**Cambridge Chemical Technologies, Inc.

***Office of Nuclear Regulatory Research, U.S. Nuclear Regulatory Commission

Prepared for

Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, DC 20555-0001
NRC Job Code N6483

Official Use Only

DRAFT

Official Use Only

ABSTRACT

This report provides an independent assessment of the risk of red oil excursions (ROEs) at the proposed mixed-oxide (MOX) fuel fabrication facility (MFFF) under construction at the U.S. Department of Energy's Savannah River site in South Carolina. The assessment is based on a review of the license application and the Integrated Safety Analysis (ISA) Summary submitted by the applicant under the requirements of 10 CFR 70. The goal of this report is to convey technical information and insights to NRC staff who are undertaking a review of the application submitted in support of an operating license. A qualitative evaluation of factors that could potentially affect ROEs is carried out in the context of the applicant's safety strategies to determine which processes are at higher risk for a ROE. The qualitative discussion is supplemented by a quantitative probabilistic risk assessment (PRA) of ROEs in various process units of the facility. Based on this limited analysis, which incorporates a large amount of uncertainty, the main contributors to ROE are identified and discussed. While the results of the risk assessment of ROEs should be considered preliminary, they do suggest that the facility is designed fairly robustly to withstand red oil events, and the risk of a ROE, in qualitative terms, may be assessed to be highly unlikely.

DRAFT

DRAFT

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT.....	iii
LIST OF FIGURES	vii
LIST OF TABLES.....	viii
EXECUTIVE SUMMARY	ix
1. INTRODUCTION.....	1-1
1.1 Background	1-1
1.2 Objectives of Study	1-3
1.3 Outline of Report	1-3
1.4 References.....	1-4
2. RISK-INFORMED DECISION MAKING (RIDM) PROCESS.....	2-1
2.1 RIDM for Fuel Cycle Facilities	2-1
2.2 Three-Region Diagram.....	2-5
2.3 References.....	2-6
3. THE RED OIL PHENOMENON	3-1
3.1 Red Oil Event Phenomenology	3-1
3.2 Chemistry of Red Oil Excursions	3-1
3.3 References.....	3-9
4. RED OIL SAFETY STRATEGY IN THE CAR AND THE LICENSE APPLICATION	4-1
4.1 CAR Safety Strategy for Red Oil.....	4-1
4.2 Post-CAR Red Oil Safety Strategy.....	4-2
4.3 Discussion of Red Oil Coping Strategies in the ISA.....	4-4
4.3.1 IROFS	4-5
4.3.2 IROFS for TBP Prevention Strategy	4-5
4.3.3 IROFS for Heat Transfer Strategy.....	4-8
4.3.4 IROFS for Evaporative Cooling Strategy	4-9
4.3.5 Defense-in-Depth	4-11
4.3.6 Normal Process Controls	4-11
4.4 References.....	4-11
5. MOX FACILITY OPERATIONS RISK RANKING.....	5-1
5.1 Process Description	5-2
5.2 Generic Risks.....	5-2
5.3 Unit Operation Risks	5-4
5.3.1 Purification Cycle – KPA	5-4
5.3.2 Solvent Recovery Unit.....	5-13
5.3.3 Acid Recovery Unit.....	5-14
5.3.4 Oxalic Mother Liquor Recovery Unit (KCD)	5-18
5.3.5 Oxalic Precipitation and Oxidation Unit (KCA)	5-25
5.3.6 Slab Settler.....	5-28

**TABLE OF CONTENTS
(Cont'd)**

	<u>Page</u>
5.4 Overall Design Strengths and Considerations	5-33
5.4.1 Design Strengths.....	5-33
5.4.2 Overall Design Considerations.....	5-34
5.5 References.....	5-35
6. RED OIL SAFETY STRATEGY – AN OVERVIEW	6-1
6.1 TBP Prevention Strategy – Component Specific Application.....	6-2
6.2 Heat Transfer Strategy – Component Specific Application.....	6-5
6.3 Evaporative Cooling – Component Specific Application	6-7
6.4 Red Oil Scenario for KPC – EV 2000.....	6-8
6.4.1 Conditions Necessary for Red Oil Excursion	6-8
6.4.2 Minimum Water-to-TBP Mass Ratio and Maximum TBP Layer Depth.....	6-10
6.5 Red Oil Scenario for KPC – TK 3000.....	6-24
6.5.1 Conditions Necessary for Red Oil Explosion in TK 3000.....	6-25
6.5.2 Conditions that Could Result in Excessive Tank Temperature Rise.....	6-26
6.5.3 ROE Event Tree for KPC – TK 3000.....	6-27
6.6 Red Oil Scenario for KPC – EV6000.....	6-32
6.7 Red Oil Scenario for KCD EV 3000.....	6-34
6.7.1 Conditions Necessary for Red Oil Excursion.....	6-34
6.7.2 Potential TBP Transfer Mechanism from KPA to KCD.....	6-35
6.7.3 Event Trees for Red Oil Excursions (ROE) in KCD-EV 3000.....	6-37
6.7.4 Description of the Event Tree Headings.....	6-37
7. SUMMARY AND CONCLUSIONS.....	7-1
7.1 Red Oil Phenomenon.....	7-1
7.2 Safety Strategies for Red Oil at MFFF	7-2
7.3 Limitations of the BNL Study.....	7-2
7.4 Qualitative Assessment of ROE.....	7-3
7.5 Quantitative Assessment of ROE.....	7-5
7.6 Conclusions.....	7-7
7.1 References.....	7-8
Appendix A Failure Rate Data, Event Trees and Fault Trees.....	A-1
Appendix B Red Oil Safety Strategy and TBP Prevention Strategy By Vessel in the AP Processing Units	B-1
Appendix C Response to the Review Comments by Dr. Dana Powers	C-1

LIST OF FIGURES

	<u>Page</u>
2-1. Three-region risk acceptance diagram.....	2-6
3-1 Necessary conditions for a red oil explosion to occur	3-2
3-2 Temperature and pressure evolutions during heating of the mixtures	3-6
5-1 AP process units	5-1
5-2 Purification cycle showing equipment layout including pulsed extractors PULS 2000, PULS 2100, PULS 2200, PULS 3000, PULS 3200	5-5
5-3 Solvent recovery cycle unit	5-13
5-4 Acid recovery unit.....	5-15
5-5 Oxalic mother liquor recovery unit.....	5-19
5-6 Oxalic precipitation and oxidation – calciner – unit	5-26
5-7 Slab settler cross-section view	5-29
5-8 Slab settler dimensions and locations of the levels of the light and heavy phases	5-31
6-1 The event tree for ROE in EV2000 due to failure of evaporative cooling under normal TBP accumulation condition	6-12
6-2 The two paths for TBP accumulation during upset conditions	6-15
6-3 The event tree for ROE initiated from pulse 2000	6-18
6-4 The event tree for ROE initiated from pulse 3200	6-19
6-5 Event tree for red oil excursion (ROE) for KPC-TK3000	6-29
6-6 Schematic diagram of KPC-TK3000	6-30
6-7 The various transfer paths of solvent to KCD-EV 3000 and the associated safety barriers that can be credited.....	6-37
6-8 Event Tree for ROE in KCD-EV 3000 due to solvent transferred by mechanical entrainment	6-38
6-9 Event Tree for ROE in KCD-EV 3000 caused by transfer of separated phase of solvent due to sever process malfunction	6-39

LIST OF TABLES

	<u>Page</u>
2-1 Event Risk Matrix	2-4
3-1 Exothermic reactions in TBP-HNO ₃ Mixtures.....	3-6
4-1 List of engineered IROFS for the red oil safety strategy	4-6
4-2 List of administrative IROFS for the red oil safety strategy	4-7
5-1 Solubility of TBP in Aqueous Nitric Acid Solutions at 25°C Recovery Cycle Unit.....	5-8
5-2 Calculation of interface heights as function of phase density	5-32
6-1 Prevention strategy IROFS, example of major prevention strategy barriers	6-4
6-2 Heat transfer strategy IROFS, example of major components.....	6-6
6-3 Evaporative cooling strategy IROFS, components applied and components protected.....	6-9
6-4 IROFS for KPA-TK9100-SMPT9100.....	6-15
6-5 Frequency of ROE at EV2000.....	6-23
6-6 A summary of ROE sequences of EV2000 scenarios.....	6-24
6-7 Instrumentation and Controls for tank TK 3000.....	6-28
6-8 Frequency of ROE Sequences under normal and upset conditions at TK3000.....	6-31
6-9 Summary of Uncertainty Analysis for ROE Sequences of TK3000 Scenario	6-32
6-10 Instrumentation and Controls for evaporator EV 6000.....	6-33
6-11 Frequency of ROE Sequences at EV 3000 (per year).....	6-42
6-12 Summary of Uncertainty Analysis for ROE Sequences of EV3000 Scenarios	6-43

EXECUTIVE SUMMARY

This study is an independent analysis of issues related to the risk of red oil excursions (ROEs) in the proposed MOX Facility (MFFF) under construction at the U. S. Department of Energy's Savannah River site in South Carolina. The assessment is based on a review of the license application and the Integrated Safety Analysis (ISA) Summary submitted by the applicant under the requirements of 10 CFR 70. The results and insights of this study could be useful to NRC staff during reviews of the MFFF License Application (LA). It is clearly understood that these results and insights related to the risk of ROEs are only meant to convey additional information and an independent perspective on risk to the NRC staff. They are not meant in any way to serve as the basis for any determinations related to facility licensing that are made under the requirements of 10 CFR 70.

The MFFF will manufacture mixed oxide (MOX) fuel consisting of plutonium dioxide, extracted from surplus weapons-grade plutonium, and depleted uranium dioxide, a byproduct of the uranium enrichment process. In the technology used in the process, a reaction can occur known as a ROE, which is an explosive, runaway nitration-oxidation reaction when the organic solvent, tri-butyl phosphate (TBP), comes in contact with concentrated nitric acid under certain conditions. ROEs have occurred in facilities, employing processes similar to MFFF, in the past, both in the U.S. and abroad. The report provides an overview of the chemistry and phenomenology of ROEs as background for the analysis of such events in the MFFF.

The safety strategy and approach for coping with the possibility of red oil events proposed by the applicant in the LA and analyzed in the ISA Summary is discussed in the study. It consists of three elements as follows: (1) Segregation of separate phase solvent (TBP) from acid bearing and heated process equipment, such as evaporators, to ensure that a separate phase of TBP does not come into prolonged contact with highly concentrated nitric acid at elevated temperatures; (2) Heat transfer strategy that relies on simple convective and radiative heat transfer mechanisms; and (3) Evaporative cooling strategy that provides for heat removal via evaporation of water in the aqueous phase in heated process vessels where some (limited) amount of TBP is expected to be present, and where the possibility of the exothermic nitration oxidation reaction exists.

A qualitative assessment of the factors that could influence the possibility of ROE has been carried out for the various process units comprising the Aqueous Polishing Unit, the only part of the MFFF where organics and acid come in contact, which can give rise to red oil excursions. Particular attention was focused on the evaporators in the acid recovery unit, the concentrates collecting tank in the acid recovery unit, and the evaporator in the oxalic mother liquor recovery unit. There is a possibility of some TBP accumulation in these units and since the evaporators are heated and contain concentrated acid, there is a higher possibility of a ROE than in other vessels and units where the environment and temperatures do not favor a ROE.

The qualitative discussion is supplemented by a quantitative probabilistic risk assessment (PRA) of ROEs in various process units of the facility. The PRA is a "limited-scope" analysis; it considers internal process deviations that could, due to equipment failures or human errors, potentially violate the success criteria of the applicant's safety strategies and eventually lead to a ROE. External hazards, such as seismic events, or internal fires were not considered as they would have greatly enlarged the scope of the study. Fault trees and event trees for the systems

and processes considered were constructed and quantified using NRC's SAPHIRE code based on the very limited data available for equipment failures and potential human errors in fuel cycle facilities. Based on this limited analysis, which incorporates a large amount of uncertainty, the main contributors to ROE are as follows: common cause failures in the venting system and operator failure to flush the system on schedule in the first evaporator of the acid recovery unit; common cause failures in the venting system and failure of operators to recognize low level alarms in the concentrates collecting tank of the acid recovery unit; and operational failures of the slab settler, sampling failures, and failure of air lift to stop process solution transfers leading eventually to ROE in the evaporator of the oxalic mother liquor recovery unit. These contributors arise from accident scenarios that mainly involve failures of the evaporative cooling strategy. Failures of the TBP prevention strategy that could arise from failures of density instrumentation and controls were also analyzed; their contribution to ROE is much lower since they involve failures of multiple barriers. The PRA provides information that is expected to be useful to the staff in their review of the license application.

The analysis performed using PRA techniques can be considered as risk-informing the qualitative analyses to assist NRC staff focus attention on areas of higher risk significance. Hence, the risk analysis methods support risk-informed decision making. However, while the results of the risk assessment of ROEs should be considered preliminary, in view of the very limited data available on equipment and human reliability in fuel cycle facilities, they do suggest that the facility is designed fairly robustly to withstand red oil events, and the risk of a ROE, in qualitative terms, may be assessed to be highly unlikely.

DRAFT

ABBREVIATIONS

AEC - Active Engineered Controls
AFS - Alternate Feedstock Source
AOV - Air Operated Valve
AP - Aqueous Polishing Process

BNL - Brookhaven National Laboratory

CAR - Construction Authorization Request
CFR - Code of Federal Regulations
CCTI - Cambridge Chemical Technologies, Inc.

DBP - Di-butyl phosphate
DFNSB - Defense Nuclear Facilities Safety Board
DOE - Department of Energy

EAC - Enhanced Administrative Controls

HAN - Hydroxyl Ammonium Nitrate
HPT - Hydrogenated propylene tetramer
HVAC - Heating, Ventilation, and Air Conditioning System
HWS - Hot Water System

IAS - Instrument Air System
ISA - Integrated Safety Analysis
ISL - Information Systems Laboratories, Inc.
IROFS - Items Relied on For Safety

KDB - Dissolution Unit
KPC - Acid Recovery Unit
KWD - Aqueous Waste Reception Unit

LA - License Application
LFL - Lower Flammable Limit
LGF - Laboratory Liquid Waste Receipt Unit

MBP - Mono-butyl phosphate
MFFF - Mixed Oxide Fuel Fabrication Facility
MOX - Mixed Oxide
MOX Services - Shaw Areva MOX Services, LLC

NPP - Nuclear Power Plant
NRC - Nuclear Regulatory Commission
NMSS - NRC Office of Nuclear Material Safety and Safeguards

KCA - Oxalic Precipitation and Oxidation Unit
KCD - Oxalic Mother Liquor Recovery Unit
KPA - Purification Cycle Unit

KPB - Solvent Recovery Unit
KWG - Off gas treatment unit
KWS - Solvent Waste Reception Unit

PDCF - Pit Disassembly and Conversion Facility
PEC - Passive Engineered Controls
PRA - Probabilistic Risk Assessment
PSCS - Process Safety Control Subsystem
PUREX - Plutonium Uranium Recovery by Extraction

QHG - Quantitative health guideline

RIDM - Risk-Informed Decision Making
ROE - Red Oil Excursions

SA - Safety Assessment
SER - Safety Evaluation Report
SSCs - Structures, Systems, and Components

TBP - Tributyl Phosphate

DRAFT

1. INTRODUCTION

The U.S. Nuclear Regulatory Commission (NRC) is in the process of licensing a facility to manufacture mixed oxide (MOX) fuel at the U.S. Department of Energy's (DOE) Savannah River site in South Carolina. MOX fuel is a blend of plutonium dioxide and depleted uranium dioxide that will be used as fuel in commercial nuclear power plants (NPPs). Depleted uranium is a byproduct of the uranium enrichment process. Plutonium dioxide will be extracted from surplus plutonium originally intended for use in nuclear weapons. The purpose of manufacturing MOX fuel will be used in meeting the goals of the DOE's Surplus Plutonium Disposition Program. Under this program, Russia and the U.S. will reduce the inventory of fissile material from nuclear weapons by each converting approximately 34 metric tons of surplus weapons-grade plutonium into MOX fuel for use in commercial NPPs. Converting the fissile material into MOX fuel and using the fuel in a commercial nuclear reactor renders the plutonium less attractive for use in nuclear weapons.

The responsibility for ensuring that the facility is designed, constructed, and operated safely resides with the license applicant: Shaw Areva MOX Services, LLC (MOX Services), a contractor to DOE, whose responsibility is to design, build, and operate the MOX Fuel Fabrication Facility (MFFF). NRC's role is to provide sufficient oversight and regulation to ensure that public health and safety, the common defense and security, and the environment remain protected. The NRC approved a Construction Authorization Request (CAR) for MFFF in 2005 and is currently in the process of reviewing the License Application (LA) submitted in 2007.

Brookhaven National Laboratory (BNL) is assisting the NRC in undertaking a review of some of the specific processes proposed to be employed at the MOX facility. This review is focused specifically on an independent evaluation of the phenomenon known as a "red oil excursion (ROE)" that can potentially occur in some of the chemical separation processes proposed to be employed at the MOX FFF. BNL's work is meant to assist NRC reviewers assess the risk significance of the red oil phenomenon. The NRC is responsible for the overall review of the LA to ensure that the facility is operated within the envelope of the applicable regulations governing safety contained in the Code of Federal Regulations (CFR), Title 10 Part 70 (10 CFR 70).

1.1 Background

The MOX facility is expected to receive plutonium feed from two sources: (1) the DOE Pit Disassembly and Conversion Facility (PDCF) located adjacent to the MOX FFF, and (2) other DOE sources, known as the Alternate Feedstock Source (AFS). The PDCF will disassemble plutonium pits from weapons and convert the material to plutonium oxide for feedstock to the MFFF, while a smaller amount of plutonium will come from AFS. PDCF feeds will contain impurities, mainly gallium, americium, and high enriched uranium, while AFS feeds are expected to contain more diverse and higher amounts of impurities [1-1]. These impurities will be removed in a three-step process consisting of dissolution, purification and conversion before the fuel can be used in a commercial NPP. The first step involves electrolytic silver-catalyzed dissolution of the plutonium dioxide powder in a nitric acid medium. The second step will be purification of plutonium by solvent extraction. The solvent is tributyl phosphate (TBP) dissolved in the diluent hydrogenated propylene tetramer (HPT). In the third step, the purified plutonium will be converted to plutonium dioxide powder using the oxalate conversion process, and calcination. The purified plutonium dioxide will be mixed with depleted uranium dioxide to form

the MOX powder. This powder is pressed and bonded into pellets through a heating process called sintering. The pellets are then loaded into corrosion-resistant thin metal tubes called fuel rods. The rods are bundled into fuel assemblies that are shipped to NPPs licensed to use MOX fuel.

MOX fuel is not currently being produced in the U.S., but European countries have been producing MOX fuel for more than 20 years. Their supply of plutonium, however, is from spent nuclear fuel rather than disassembled nuclear weapons.

In September 2000, the U.S. and Russia signed an agreement to reduce their respective stockpiles of surplus plutonium. The DOE evaluated the different strategies to dispose of this material. Under the DOE Surplus Disposition Program, approximately 34 metric tons of surplus weapons-grade plutonium are planned to be converted into MOX fuel to be used in commercial NPPs.

Facilities such as the MFFF that employ chemical separations technology to purify plutonium are vulnerable to a hazard known as the "red oil phenomenon," an explosive nitration-oxidation chemical reaction which has occurred before in older fuel reprocessing facilities. BNL earlier carried out an analysis [1-2] of the specific hazard of ROEs based on the design of the facility revealed in the CAR [1-3]. That analysis was based on the limited design information available in the CAR and included a preliminary risk assessment of systems vulnerable to the red oil hazard.

The objective of the earlier study was to provide technical assistance using the risk-informed decision making (RIDM) framework to the Division of Fuel Cycle Safety and Safeguards personnel in the area of licensing reviews of new facilities, such as the MOX facility. Specifically, the issues relating to the risk of ROEs were analyzed in this study, based on the CAR design, to provide NRC staff with some in-depth information that would be useful in making decisions related to the issuance of a possession and use license for a MOX facility.

The report identified and described a number of processes, specified in the CAR for which prevention of ROEs is important. The report identified parameters controlled, the controls, and relevant set points. The sequences of events that would lead to ROEs were identified and delineated with event trees and the top events by fault trees using standard failure mode and effects analysis methodologies. The goal was to identify and rank the most risk significant systems and operations in the MOX facility for ROEs and obtain an approximate point estimate of the ROE frequency based on the system design revealed in the CAR. This assisted the NRC reviewers in determining the relative risk significance of various systems and processes. The risk insights obtained from this work were meant to help the NRC staff involved with reviewing the LA carry out a more risk-informed assessment of the design proposed by the applicant. In carrying out the analysis, appropriate comparisons were made with the findings of both the CAR and the NRC's Final Safety Evaluation Report (SER) [1-4].

The work performed in Reference [1-2] followed the general approach outlined in the guidance document for risk-informing the nuclear waste and materials arenas: "Risk-Informed Decision-Making (RIDM) for Nuclear Material and Waste Applications" [1-5]. The RIDM approach has been designed to focus NRC resources on areas commensurate with their safety, provide a framework for using risk information, and where amenable, use risk information to provide flexibility for making decisions and managing the workload in NRC more effectively.

In addition to providing a risk-informed perspective of the work that had already been performed by the applicant in the CAR (and by NRC in the SER), the tools and methods developed were expected to be useful adjuncts to the safety evaluation related to the red oil phenomenon that would be associated with the NRC review of the Integrated Safety Analysis (ISA) Summary, and other documents submitted by the applicant in support of the possession and use LA.

1.2 Objective of Study

The objective of the study presented in this report is to provide an independent assessment of the risk significance of the red oil phenomenon in the MOX FFF based on the design contained in the application submitted by the applicant for a possession and use license. The assessment takes into account the safety strategy for dealing with the red oil phenomenon that is outlined in the ISA Summary [1-6] submitted by the applicant along with the LA. It is stated by the applicant that the current strategy for preventing red oil events has several differences from the one that was adopted earlier in the CAR, which was reviewed by BNL in Reference [1-2]. The risk significance of potential red oil events provides a source of additional information expected to be useful to NRC staff in the context of determining whether the design meets the qualitative likelihood criteria of 10 CFR 70.61 for events that have a high consequence for facility workers.

1.3 Outline of Report

The remainder of this report is comprised of the following chapters. Chapter 2 provides a brief overview of the risk-informing process in the context of the performance criteria established in 10 CFR 70.61 and their relation to red oil events. Chapter 3 contains an overview of the red oil phenomena based on a review of the literature applicable to extraction facilities, such as the MOX FFF. Chapter 4 reviews the strategies proposed by the licensee for dealing with red oil events. Chapter 5 provides a description of the relevant process units within the MOX Facility that are susceptible to ROEs and contains a qualitative discussion of the risk of red oil in each process unit taking into account the safety analysis and safety strategy with regard to red oil provided in the ISA Summary. Chapter 6 provides a failure modes and effects analysis including fault trees and event trees of selected ROE scenarios and a point estimate of the ROE frequency for the most risk significant process units based on the design details presented in the ISA. Chapter 7 provides a summary of the work performed and outlines the major uncertainties that impact the results presented. Appendix A provides data and assumptions and a detailed list of the fault trees and event trees used to carry out a probabilistic risk assessment (PRA) of the process units selected for detailed analysis. Appendix B contains a list of all the equipment and vessels protected by the three strategies proposed by the applicant (TBP prevention, heat transfer, and evaporative cooling) for guarding against ROEs. Finally, Appendix C contains a detailed response by the BNL team to the comments made by Dr. Dana Powers of the Advisory Committee on Reactor Safeguards on an earlier draft of the BNL report.

1.4 References

- 1-1. Shaw Areva MOX Services, LLC, "Mixed Oxide Fuel Fabrication Facility License Application," Revision December 17, 2007.
- 1-2. Brookhaven National Laboratory, "Risk Assessment of Red Oil Excursions in the MOX Facility," BNL-MOX-2007-001, March 2007.
- 1-3. Duke Cogema Stone & Webster, "Mixed Oxide Fuel Fabrication Facility Construction Authorization Request," February 2005.
- 1-4. U.S. Nuclear Regulatory Commission, "Final Safety Evaluation Report on the Construction Authorization Request for the Mixed Oxide Fuel Fabrication Facility at the Savannah River Site, South Carolina," NUREG-1821, March 2005.
- 1-5. U.S. Nuclear Regulatory Commission, "Risk-Informed Decision-Making for Nuclear Material and Waste Applications," Draft for Trial Use, ADAMS Accession No. ML042730524, May 11, 2005.
- 1-6. Shaw Areva MOX Services, LLC, "Integrated Safety Analysis Summary," December 17, 2007.

DRAFT

2. RISK-INFORMED DECISION MAKING (RIDM) PROCESS

2.1 RIDM for Fuel Cycle Facilities

The U.S. NRC Office of Nuclear Material Safety and Safeguards (NMSS) is increasing the use of risk insights and information (i.e., risk-informing) in the nuclear materials and waste arenas. Risk insights and information should increase NMSS's efficiency and effectiveness in its regulatory processes: of rulemaking, licensing, inspection and enforcement. SECY-04-0182 [2-1] and its associated Staff Requirements Memorandum provided information and guidance on the status of risk-informing processes within NMSS. Further guidance for RIDM was developed by NMSS in Reference [2-2], which has recently been updated [2-3].

The essential elements of a risk-informed process are:

1. Performing a risk assessment that is suitable to the safety or licensing issue in question,
2. Obtaining or adapting relative measures of safety (also referred to as risk guidelines in the RIDM) in terms of the metrics calculated in the risk assessment,
3. Using a decision algorithm to help guide choices in terms of the outcomes of the risk assessment.

Risk measures or guidelines are one element of the overall RIDM process; they serve as a benchmark or yardstick to evaluate the significance of the change in risk due to implementation of the issue or regulatory action alternative and are used to guide a RIDM process. Quantitative guidelines do two important things: (1) establish the quantitative metrics for informing safety decisions, and (2) provide the measurement scale for determining the level of risk that exists. Hence, risk guidelines can be used to inform decisions associated with reducing unnecessary conservatism in purely deterministic approaches, and/or can be used to identify areas with insufficient conservatism in deterministic analyses and provide the supporting information for identifying the potential need for regulatory actions.

In the Guidance for RIDM for the Nuclear Materials and Waste Arenas [2-2], six draft quantitative health guidelines (QHG) are proposed. The formulation in terms of health guidelines was done because it was desirable to have a framework that was consistent with the reactor counterpart which was formulated in terms of the Reactor Safety Goals in the Commission's Safety Goal Policy Statement of 1986 [2-4]. The six draft QHGs covering the risks of early fatality, latent cancer fatality, and severe injury for both the public and the workers are provided in Reference [2-2], which contains a detailed discussion of the rationale for (and the bases underlying) the chosen values of the various QHGs.

For fuel cycle facilities, 10 CFR 70.61 [2-5] provides regulatory requirements in terms of performance criteria. These criteria require the applicant to analyze each credible event in terms of both likelihood and consequences. The likelihood is expressed in qualitative terms, i.e., "highly unlikely" and "unlikely". The consequences, radiological doses, and chemical exposures, are expressed in quantitative terms.

The requirements of the performance criteria in 10 CFR 70.61 are stated as follows:

The risk of each credible high-consequence event must be limited. Engineered controls, administrative controls, or both, shall be applied to the extent needed to reduce the likelihood of occurrence of the event so that, upon implementation of such controls, the event is highly unlikely or its consequences are less severe than those of high consequence events. High consequence events are those internally or externally initiated events that result in:

- (1) *An acute worker dose of 1 Sv (100 rem) or greater total effective dose equivalent;*
- (2) *An acute dose of 0.25 Sv (25 rem) or greater total effective dose equivalent to any individual located outside the controlled area;*
- (3) *An intake of 30 mg or greater of uranium in soluble form by any individual located outside the controlled area identified pursuant to paragraph (f) of this section; or*
- (4) *An acute chemical exposure to an individual from licensed material or hazardous chemicals produced from licensed material that:*
 - (i) *Could endanger the life of a worker, or*
 - (ii) *Could lead to irreversible or other serious, long-lasting health effects to any individual located outside the controlled area. (If an applicant possesses or plans to possess quantities of material capable of such chemical exposures, then the applicant shall propose appropriate quantitative standards for these health effects).*

The risk of each credible intermediate-consequence event must be limited. Engineered controls, administrative controls, or both shall be applied to the extent needed so that, upon implementation of such controls, the event is unlikely or its consequences are less than those of intermediate consequence events. Intermediate consequence events are those internally or externally initiated events that are not high consequence events that result in:

- (1) *An acute worker dose of 0.25 Sv (25 rem) or greater total effective dose equivalent;*
- (2) *An acute dose of 0.05 Sv (5 rem) or greater total effective dose equivalent to any individual located outside the controlled area;*
- (3) *A 24-hour averaged release of radioactive material outside the restricted area in concentrations exceeding 5000 times the values in Table 2 of Appendix B to Part 20; or*
- (4) *An acute chemical exposure to an individual from licensed material or hazardous chemicals produced from licensed material that:*
 - (i) *Could lead to irreversible or other serious, long-lasting health effects to a worker, or*
 - (ii) *Could cause mild transient health effects to any individual located outside the controlled area.*

In addition to complying with paragraphs (b) and (c) of this section, the risk of nuclear criticality accidents must be limited by assuring that under normal and credible abnormal conditions, all nuclear processes are subcritical, including use of an approved margin of subcriticality for safety. Preventive controls and

measures must be the primary means of protection against nuclear criticality accidents.

Table 2-1, taken from the MOX FFF LA [2-6], shows that in order to meet the requirements of Part 70.61, high consequence events need to be made highly unlikely and intermediate consequence events need to be made at least unlikely through the application of items relied on for safety (IROFS). The IROFS consist of passive controls, active engineered controls (AEC), and administrative controls whose application is intended to reduce the likelihood of an identified event to an acceptable category as shown in Table 2-1. The ISA Summary [2-7] identifies the IROFS for each class of accident events. The following qualitative definitions of likelihood are provided in Chapter 5, Section 5.2.2.5 of the ISA Summary:

- Not Unlikely – events that may occur during the lifetime of the facility.
- Unlikely – events that are not expected to occur during the lifetime of the facility or events originally classified as Not Unlikely to which sufficient IROFS are applied to reduce their likelihood to an acceptable level.
- Highly Unlikely – events originally classified as Not Unlikely or Unlikely to which sufficient IROFS have been applied to reduce their likelihood to an acceptable level.

The ISA Summary indicates that “in applying the above definitions to address the performance requirements of 10 CFR 70.61, initiating events are assumed to be not unlikely. Postulated credible intermediate or high consequence events are made highly unlikely based on the application of IROFS features or controls without crediting the likelihood of the initiating event.” Events that are defined as “not credible” are those: (1) natural phenomena or external events with a very low initiating frequency, (2) process deviations that consist of many unlikely human actions that have no motive, and which have never occurred in a fuel process facility, and (3) process upsets that are not possible or extremely unlikely based on physical laws. In Table 2-1, the qualitative definitions of likelihood and the definition of “credible” are consistent with, and based on, the definitions contained in the MOX FFF Standard Review Plan [2-8].

The LA states that;

“For the facility worker, conservative qualitative consequences were used. Consequences were categorized as high (H), intermediate (I), or low (L) based on the three severity levels; the facility worker is considered to be located inside the MFFF, near a potential accident. Radiological consequences to the facility worker are qualitatively determined. Facility worker consequences are qualitatively determined based on the material released, the release mechanism, and the location of the worker relative to the release. In most cases, events involving an airborne release of plutonium or americium are judged to have high consequences to the facility worker and IROFS are applied.”

A ROE that leads to a breach of a vessel or other equipment in a process unit is, in principle, a high-temperature, high-pressure release. Such a release is a high consequence event for a facility worker and, in terms of the performance criteria of 70.61, each ROE scenario or sequence would have to be shown to be “highly unlikely” in qualitative terms.

Table 2-1 Event Risk Matrix.

CONSEQUENCE	High (3)	3 No IROFS Applied	6 IROFS Applied	9 IROFS Applied
	Intermediate (2)	2 No IROFS Applied	4 No IROFS Applied	6 IROFS Applied
	Low (1)	1 No IROFS Applied	2 No IROFS Applied	3 No IROFS Applied
		Highly Unlikely (1)	Unlikely (2)	Not Unlikely (3)
		LIKELIHOOD		

(Based on Table 5.1-2 of MFFF LA)

The present report provides the steps needed for the development of a risk assessment for ROEs in the MOX facility. This begins with a systematic search for conditions and events that could potentially lead to ROEs in the various process units of the facility. It is then followed by the development of scenarios for such events in terms of event trees and the construction of logic models via fault trees for each of the top events in the event tree. The level of detail of the risk assessment is limited by the resources and time available to conduct the assessment as well as the availability of data and information at the system, component, and procedure level for a new facility. It is understood that the frequency of ROEs based on the risk assessment is meant to provide an independent perspective on risk to the NRC reviewer and is not meant to offer any determination of facility licensing which is made under the requirements of 10 CFR 70.

The Standard Review Plan for the MOX Facility, NUREG-1718 [2-8], provides guidance to the NRC staff on the notions of *unlikely* and *highly unlikely* that are introduced in 10 CFR 70.61. Chapter 5 of NUREG-1718 provides acceptance criteria for qualitative definitions of likelihood. While the regulation does not require a quantitative determination of likelihoods, NUREG-1718 also provides acceptance criteria and some guidelines for quantitative definitions of likelihood. It is stated in NUREG-1718 that, "the quantitative guidelines...are derived from safety performance goals for the whole industry", not one specific facility. The numerical guidance in Reference [2-8] is provided to inform the NRC staff reviewer. 10 CFR 70.61 requires that intermediate consequence events be rendered unlikely and high consequence events be rendered highly unlikely. This is consistent with the idea of an iso-risk line, where risk is regarded as probability multiplied by consequence. In the case of the MFFF, the licensee chose to apply the qualitative definitions of likelihood.

Thus, the evaluation of the frequency of a ROE and the worker prompt fatality draft risk guideline can be useful in risk-informing an NRC reviewer regarding the issues related to acceptability of red oil scenarios and measures employed to prevent or mitigate them. One approach is to use a three-level decision diagram as described in Reference [2-2] and discussed below.

2.2 Three-Region Diagram

Reference [2-2] provides a discussion of the risk to individuals from a regulatory action that is based on a concept of three regions of risk to individuals:

1. If a proposed action results in risk to individuals that are judged to be too high, this may be sufficient grounds to reject it.
2. If the resulting level of risk to individuals is judged to lie in the tolerable region (and other factors are adequately addressed), then alternative actions should be preferred based on highest net cost-benefit.
3. Proposed new requirements to reduce risk, when it is already in the negligible risk region should normally not be pursued.

Reference [2-2] indicates that the above principles embodied in the three-region decision framework can be applied to managing risk from accidents or unanticipated events (such as ROEs). This risk involves both the frequency and/or probability of accident occurrence for each scenario, as well as the consequence that would occur. Since there are multiple possible accident scenarios, risk is evaluated as the sum over all scenarios of the product of frequency and consequence (or the probability of fatality given that level of consequence). For the red oil events the risk would be evaluated by summing over all possible ROEs in the facility that can lead to the selected consequence, e.g., a worker fatality. Thus, in the three-region framework, risk is often expressed as frequency of fatality. However, Reference [2-2] states that unlike routine doses under 10 CFR Part 20, the Commission has not ascribed generally applicable numerical limits on risk due to accidents. The negligible level of risk is useful as a screening tool. Negligible risk levels are well below the regulatory limit levels of risk, and represent an insignificant addition relative to average normal risks.

The three-region risk diagram displayed in Figure 2-1 is a conceptual representation of these decision considerations. As indicated in Reference [2-2], the "lines" separating the regions of unacceptable, tolerable, and negligible (or insignificant) risk are not precise but take into account uncertainties that impact the risk. Such uncertainties are often accounted for by incorporating considerations related to defense-in-depth, such as levels of diversity and/or redundancy, and safety margins or by prescribing conservative methods for calculating and analyzing risk.

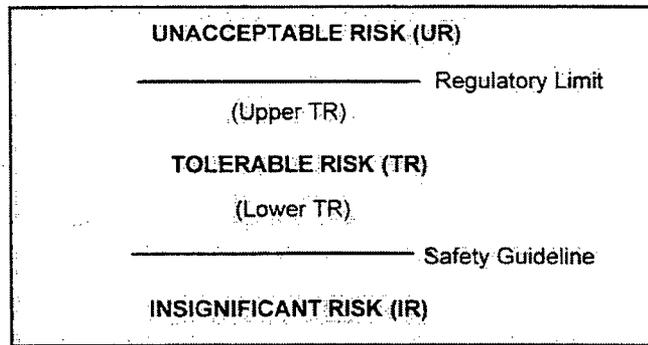


Figure 2-1. Three-region risk acceptance diagram.

This diagram divides the risk space for any applicable health risk metrics (public or worker acute fatality, etc.) or equivalent surrogate risk metrics into three regions: an unacceptable risk region, a tolerable risk region, and an insignificant risk region. The lower line shown in Figure 2-1 that separates the insignificant risk region from the tolerable risk region corresponds to the QHG below which there is no measurable benefit of reducing the risk further. As discussed in Reference [2-2], the upper line corresponds to the risk implication of the regulatory limit that separates the unacceptable risk from the tolerable risk region. The tolerable risk (TR) range is further regarded to be comprised of two regions, an upper TR (UTR) range and a lower TR (LTR) range.

This can be helpful in the consideration of the impact of uncertainty on the calculated values of the risk.

The risk-informed decision algorithm process based on the QHGs outlined in Reference [2-2] focuses on the calculated mean values of the risk metrics. As discussed above, in making decisions with the aid of this diagram, it is very important to also give due consideration to factors such as defense-in-depth and safety margins, and assure that they are maintained throughout the risk acceptance process.

It is clearly understood that the frequency of a ROE and the various draft QHGs that are applicable are meant only to provide additional information and an independent perspective on risk to the NRC reviewer. They are not meant to serve as the basis for any determinations related to facility licensing which is made under the requirements of 10 CFR Part 70.

2.3 References

- 2-1. U.S. Nuclear Regulatory Commission, "Status of Risk-Informed Regulation in the Office of Material Safety and Safeguards," SECY-04-0182, October 7, 2004 and Staff Requirements Memorandum, January 18, 2005.
- 2-2. U.S. Nuclear Regulatory Commission, "Risk-Informed Decision-Making for Nuclear Material and Waste Applications," Draft for Trial Use, ADAMS Accession No. ML042730524, May 11, 2005.

- 2-3. U.S. Nuclear Regulatory Commission, "Risk-Informed Decision Making for Nuclear Material and Waste Applications," Revision 1, February 2008.
- 2-4. U.S. Nuclear Regulatory Commission, "Safety Goals for the Operation of Nuclear Power Plants Policy Statement," Federal Register, Vol. 51, p. 30028 (51 FR 30028), August 4, 1986.
- 2-5. U. S. Code of Federal Regulations, 10CFR70.61, <http://www.gpoaccess.gov/cfr/index.html>.
- 2-6. Shaw Areva MOX Services, LLC, "Mixed Oxide Fuel Facility License Application," Revision, December 17, 2007.
- 2-7. Shaw Areva MOX Services, LLC, "Integrated Safety Analysis Summary," December 17, 2007.
- 2-8. U.S. Nuclear Regulatory Commission, "Standard Review Plan for the Review of an Application for a Mixed Oxide (MOX) Fuel Fabrication Facility," NUREG-1718, August 2000.

DRAFT

3. THE RED OIL PHENOMENON

3.1 Red Oil Event Phenomenology

The purification and/or separation of metals in the MFFF is accomplished by a process known as liquid-liquid extraction, or solvent extraction, that is also commonly used in the chemical and petrochemical industries. In this process, one or more components, e.g., metal impurities, are transferred between two immiscible liquid phases, typically an organic phase and an acidic aqueous phase. The solvent proposed to be used in the MOX facility is TBP diluted in an organic matrix to improve the physical characteristics of the organic phase. The diluent is HPT that is similar to dodecane (a relatively inert and radiation resistant organic chemical); it reduces the viscosity and density of the organic phase to improve phase separation and also acts to lower actinide concentration in the liquid and hence reduce criticality concerns.

This report focuses on events that may lead to the formation of red oil and the explosive decomposition of organic nitration and/or oxidation reaction products within the aqueous polishing (AP) process where plutonium is purified by solvent extraction. Red oil is defined as a substance of varying composition formed when organic constituents react with nitric acid. In the AP process, these substances may form by reactions of TBP, its decomposition products, and impurities in the diluent with nitric acid. Previous studies have shown that red oil decomposition is exothermic and generates a relatively large amount of gas, leading to the risk of a runaway reaction(s) and overpressurization.

According to official sources, red oil events have occurred three times in DOE facilities: at Hanford in 1953, at Savannah River in 1953 and then again at Savannah River in 1975 [3-1]. A red oil event occurred at the Tomsk facility in Russia in 1993 [3-2] and at a facility in Canada [3-3]. A red oil event also occurred at Oak Ridge in 1959 [3-4]. A recent report issued by the Defense Nuclear Facilities Safety Board (DNFSB) [3-1] on ROEs summarizes the events that have occurred in the extraction operations at Savannah River and Hanford and the accident at the Tomsk plant in Russia. From 1953 until the present, a period of roughly 50 years, the six red oil events which have occurred establish a gross red oil event frequency of approximately 0.1 per year.

The report issued by the DNFSB identifies the issues involved, and controls needed, to prevent red oil explosions within DOE facilities. As defined in the DNFSB report, red oil is a substance of non-specific composition that can be created when an organic phase consisting of TBP and diluent in contact with concentrated nitric acid is heated above 122°C (251.6°F) under reflux (a stream of condensed overheads returned to the boiling liquid for increasing or decreasing the concentration of one or more components in the boiling liquid). The red color is believed to be due to nitrated organic species as well as the evolution of nitrogen dioxide, a gas with a reddish-brown color.

3.2 Chemistry of Red Oil Excursions

Organic matter in contact with nitric acid may lead to the formation of red oil. The rate of formation and possible decomposition of red oil and/or organic components, such as TBP, is enhanced by:

1. Nitric acid concentration (in typical reprocessing facilities, this concentration varies from low acidity to about 13.6M; the limit is the nitric acid/water azeotrope: 68.4 wt % nitric acid at a boiling temperature of 122°C [251.6°F])
2. Temperature (normal operating temperatures, except in the calciner are maintained below 130°C [266 °F])
3. Residence time (depending on the equipment involved, this may vary from a few minutes to many days for storage)
4. Efficiency of contact (mass transfer)
5. Radiation dose – leading to possible radiolytic decomposition of organics to form more reactive species.

The conditions that contribute to a red oil event are shown in Figure 3-1. Adequate venting to remove the heat generated in the exothermic reaction and prevent overpressurization is important for evaluating the potential consequences of a ROE.

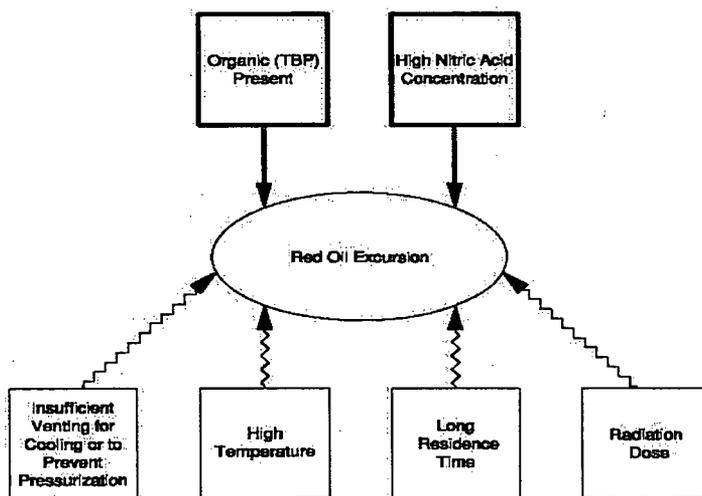


Figure 3-1. Conditions for a red oil explosion to occur

Organics are referred to in general terms in this report; the organics which are mostly of concern are TBP, TBP nitrates, TBP decomposition products, such as dibutyl phosphate (DBP), monobutyl phosphate (MBP), butanol and impurities in the diluent. Additionally, because most of the solvent is recycled within the process, generation or input of even a small amount of impurities will tend to build up unless special care is taken to monitor and purge such buildup. Unlike the class of chemicals mentioned above, contact between the organic diluent used and nitric acid is not considered as a possible source of unwanted reactions, because the organic diluent used is HPT, which does not react with nitric acid at the temperatures normally encountered in this process.

The amount of red oil depends on:

1. The rate of formation
2. The area of contact between the organics and the acid phase
3. Length of contact time between the two phases.

The oxidation of TBP and its decomposition products, i.e., red oil formation, takes place over a wide range of temperature, with the rate dependent on temperature, acid concentration; radiolysis, etc., as illustrated in Figure 3-1. At lower temperatures, below about 60°C, the heats of reaction and the volumes of gases evolved are generally small. What is of concern is the very energetic exothermic decomposition reaction and associated overpressurization, the so-called self-heating runaway reaction, which has been observed at higher temperatures.

The risk of red oil formation and decomposition exists in any area that contacts TBP and other organics with an oxidizing agent, such as nitric acid, or that receives organic material that may have previously contacted nitric acid or aqueous material that may have come in contact with organic compounds. The undesirable reactions are promoted by the presence of unstable organic constituents, such as TBP decomposition products, high nitric acid concentration, high temperature, long residence time, the catalytic effects of metals in solution such as plutonium, zirconium, and uranium on the reaction rate, the radiolytic dissociation of organics present, and the decay heat associated with plutonium and americium. Severity of events, such as rupture of primary containment, is increased by inadequate heat removal and inadequate vent area.

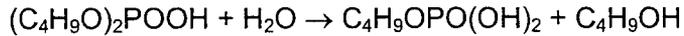
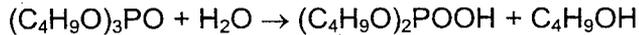
Previous studies, e.g., Hyder [3-5], indicate that red oil exothermic decomposition is negligible below 130°C (266°F). For example, the DNFSB Technical Report [3-1, page 6-1] states that "maintaining of temperature of less than 130°C is generally accepted as a means to prevent any red oil explosions." While this may be a reasonable criterion for process equipment where residence times tend to be in minutes or less, and the material is renewed frequently, it may not be so in tanks and dead legs in the piping system. Conditions for red oil reactions are likely to be present for days, even months, in such locations, as was the case at the Tomsk facility.

It is worth noting that in such facilities, as indicated in the DNFSB report [3-1] tanks and dead legs in the piping system are unlikely to have sufficient heat removal capabilities or volatile components to efficiently remove heat generated by any exothermic reactions. Exothermic reactions could lead to an uncontrolled temperature rise even in situations where the initial temperature is quite low. Furthermore, the areas in which these stagnant fluids can collect are often difficult to assess, thus making it impossible to correctly measure the temperature in all such places.

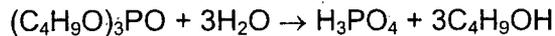
In mixed systems, if TBP in the aqueous phase is consumed by any reaction, it will be replaced (by mass transfer from the interface) with additional TBP from the organic phase. Whether it slows down the overall rate of degradation will depend on total interfacial area and mass transfer flux in comparison to the reaction rate. In emulsions, for example, there may be sufficiently high mass transfer rate to replenish material lost due to reaction. The initial phase of the reaction is likely to be strongly dependent on the area and thickness of the interface between the aqueous and organic phases.

Possible reactions between TBP and nitric acid that include possible TBP decomposition products are described in NRC's SER [3-6] and the MFFF ISA Summary [3-7]. These reactions can be summarized as follows:

- Hydrolysis reactions – TBP to DBP to MBP and eventually 3 mols of butanol and 1 mol of phosphoric acid:



which can be summarized as:



- De-alkylation reaction: TBP may undergo de-alkylation with nitric acid as follows.

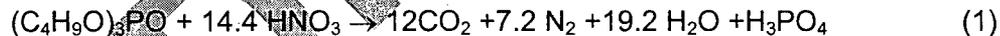


- Pyrolysis, which mostly occurs at higher temperature and where there is no water present.

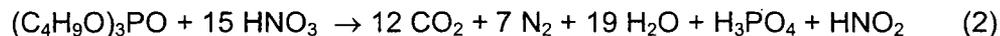
In addition, butanol, butyl nitrate, and TBP nitration/oxidation reactions are significant sources of energy and gas evolution.

It is difficult to predict the extent to which each of the above reactions will proceed under various conditions of nitric acid concentration, organics to nitric acid ratio, amount of dissolved nitrogen oxides, temperature, residence time and mass and heat transfer efficiency – which affects the temperature rise.

Hyder [3-5] proposes the following reaction that assumes complete oxidation of TBP to carbon dioxide, phosphoric acid, and water:



The above reaction generates about 1540 Kcal/mole TBP; this is approximately 16 times higher than the reaction energy derived by Eisenhower et al. [3-8] based on experimental measurement by Nichols [3-9]. The ISA Summary [3-7, page 5.3.6-61] considers a different stoichiometry for the TBP oxidation mechanism:



The heat generated from this reaction is approximately 1689 Kcal/mole TBP, making the reaction energy higher than the reaction mechanism proposed by Hyder [3-5]. Similarly, the moles of gas evolved from the second mechanism are greater than the first mechanism, making it an even more conservative design reaction. However, both Hyder and the ISA Summary remark that the above theoretical reaction energy evolved is based on the assumption that the TBP undergoes complete oxidation, which is overly conservative. According to Hyder, the extent of reaction is limited by the concentration of nitric acid (i.e., the oxidizer) in the organic phase, so that only a small fraction of the oxidant that is required to fully oxidize the TBP is available. Further, in an open system,

if the reaction produces intermediate products that evaporate the amount of reaction heat is further reduced.

For safety analyses, one may consider the extent of oxidation, which depends on the amount of TBP that is present, as an uncertain parameter and perform a range of sensitivity calculations, from the bounding energy released in the reaction represented by the equation above to the energy release assumed by Eisenhower, to determine the amount of heat and the volume of gases evolved. For venting calculations the bounding condition is the reaction(s) that will produce the maximum volume of gas. For practical applications, Hyder [3-5] explains why the lower heat evolution, with some relatively minor corrections is appropriate to use for design calculations.

However, to consider the bounding condition, the vent calculations for the Hyder postulated reaction of Equation (1) would have to be sized for total moles of gas generated by the above reaction plus moles of volatile material that will vaporize as a result of the reaction heat. Moles of material vaporized will depend on molar heat of vaporization. It is worth noting that molar heat of vaporization of butanol, approximately 10 Kcal/gm-mole [3-10], is about the same as that of water, which means that the amount of moles vaporized, and, therefore, gas volume will be the same.

Nazin et al. [3-11] recently performed experiments on the kinetic features of the thermochemical degradation of the two-phase systems TBP-HNO₃ and 30% TBP in dodecane-HNO₃ heated in a sealed vessel. The experiments were carried out over temperatures ranging from 120 - 170°C (248 - 338°F) and the nitric acid concentration varied from 1.5 M to 14 M. The temperatures were monitored via thermocouples in the organic phase, at the interface, and in the aqueous phase at various distances from the interface. In this way, a more complete map of the temperature dependence of the reaction in different phases was obtained.

The exothermic reaction rate is influenced by (1) heat transfer to the environment, (2) mass transfer of the oxidant NO₂ from the aqueous and gas-vapor phases to the organic phase, and (3) other factors like evaporation, mixing of the phases and gas liberation. The temperature measurements reveal that the reaction starts not only in the bulk of the organic phase but also at the interface of the two phases. If the exothermic heat in the organic phase produced by the oxidation reaction is greater than the heat loss through the walls of the vessel and to the aqueous phase so as to result in a progressive temperature rise, the oxidation process is accelerated and there is an abrupt step increase in temperature and pressure within the vessel as shown in Figure 3-2 (taken from Figure 2 of Nazin et al.). If the heat losses are greater than the heat evolved, the self-heating rate is low and the oxidation of the organics remains incomplete as shown by the amount of gaseous products generated in the reaction. Nazin et al. remarked that the difference between heat gain and loss in the exothermic reactions occurring in the two phase systems at relatively low nitric acid concentration "is very sensitive to various factors, so that insignificant variations in the process conditions can change remarkably the thermal oxidation rate and extractant conversion."

The experimental results of Nazin et al. on the onset and maximum temperature of the reaction, the mean heat up rate and the maximum pressure generated as a function of nitric acid concentration are shown below in Table 3-1. These data show the

acceleration of the reaction and the lowering of the onset temperature as the nitric acid concentration increases.

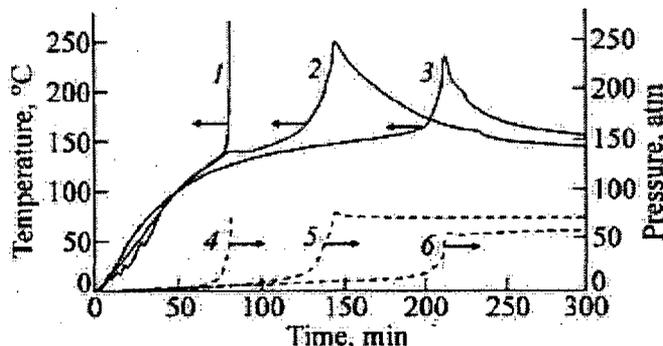


Figure 3-2. (1-3) Temperature and (4-6) pressure evolutions during heating of the mixtures of 7.8M HNO₃ with (1, 4) 100% TBP, (2, 5) 30% TBP in dodecane, and (2, 6) 100% dodecane. Thermostat temperature 170°C (338°F) and organic to aqueous phase volume ratio 1:3. (Source: Nazin et al. [3-11]).

Table 3-1. Exothermic reactions in TBP-HNO₃ mixtures.

HNO ₃ conc in aqueous phase, M	Onset of exothermic reaction (°C)	Max temp obtained (°C)	Mean heat up rate (°C/min)	Max pressure (atm)
1.5	142 - 145	168	-	29
3.0	145 - 150	187 - 230	1.2 - 2.6	21.5 - 68
5.0	145	192 - 255	2.1 - 11.5	20 - 87.5
7.0	137 - 140	300	16	100
10.0*	135	> 265*	> 14*	> 90*
14.0*	123	> 123*	-*	-*

*Break of safety membranes of the autoclave precluded measurements (Source: Nazin et al. [3-11])

The effects of irradiation on the onset temperature of the exothermic reaction were also studied, and it was observed that the onset temperature decreased and the intensity of the reaction was higher. In an irradiated mixture similar to what was believed to be present at the time of the Tomsk accident, the exothermic reaction was observed to start at temperatures ranging from 85 - 95°C (185 - 203°F), well below what was observed in the non-irradiated mixtures.

Nazin et al. go on to conclude: "it is not improbable that in actual extraction systems exposed to the combined impact of oxidizing agents, temperature and radiation, the onset temperature of hazardous exothermic reactions can well be comparable with not only the evaporation temperature of nitric acid solutions but also with the maximal temperatures realized in the extraction recovery stages. *Note that extraction systems*

can approach these temperatures by virtue of both an external heating source and inner self heating produced by radioactive decay."

Paddleford and Fauske [3-12] report the results of a number of experiments on TBP-nitric acid mixtures to determine runaway reaction temperature, pressure rise and safe venting practices. Heat generation from exothermic reactions and decompositions involving TBP and other organics is proportional to the reaction rate. Thus, the heat generation relationship can be represented by an Arrhenius equation with appropriate coefficients. The activation energy in the Paddleford-Fauske experiments is reported to be about 26,800 cal/(g-mole-K). In other words, the rate at 130°C (266°F) will be about 40 times higher than at 90°C (194°F). The above relationships, plus thermodynamic data (such as heat of vaporization for various compounds, vapor pressure relationships, heat capacity, etc.), given the heat removal capacity of the equipment in question, would allow one to calculate the net temperature and pressure rise as the result of the relevant reactions.

The ISA Summary states that a "semi-empirical model describing the heat generation for TBP/nitric acid was developed to specifically account for conditions present in the AP process." This model [3-13] is stated to be based on data from "over 80 individual experiments" that examined the impact of temperature, nitric acid concentration, and the catalytic effects of plutonium, uranium, and zirconium concentration on the reaction rate constants. The heats of reaction were established and used to develop the criteria for the heat transfer and evaporative cooling strategies for protecting against ROEs.

A supporting document provided by the licensee [3-14] on TBP-nitric acid systems contains criteria for effective evaporative cooling of the nitration-oxidation reaction based on a large-scale review of the existing literature and experimental data from a variety of sources. It is stated that the energy evolved in chemical degradation of TBP and the subsequent oxidation of the degradation products and the rate of degradation is uncertain as it is a very complex reaction. In the author's view, the goal of the exercise was to obtain a conservative upper bound, based on the assumption of a 100% TBP organic phase, for the reaction heat that would be generated. This heat evolved was then compared for an open (vented) system with the heat that could be carried away by the evaporation of the reactants, thus providing a measure of the effectiveness of the strategy of evaporative cooling as a means of removing the energy generated by the oxidation reaction.

The experimental data cited for the open system are from the experiments done by Tashiro (cited in Ref. [3-14]) in a kinetic study at 90°C (194°F) of 3:1 volume ratio of aqueous (10M HNO₃):TBP mixture plus 3 wt % butanol under atmospheric pressure. These data yield a heat of reaction of approximately 237 kcal per mole of TBP reacted. (This is a little less than one-sixth of the energy generated from the complete oxidation of TBP based on the Equation (2) cited above from Hyder's data and about one-seventh of the amount cited in Equation (3) above). This heat of reaction can be equated to the latent heat of evaporation of water, approximately 540 kcal per kg at 100°C and atmospheric pressure, to provide a rough estimate of the quantity of water needed to provide evaporative cooling. The quantity of water needed depends upon the concentration of nitric acid, because the energy production due to TBP degradation is a function of nitric acid concentration and its rate decreases with decreasing acid concentration. The solubility of nitric acid in TBP is low, and since the nitric acid/water is

evaporated around the azeotropic limit of 122°C, the limiting reagent for heat generation would be HNO₃.

The calculation carried out in Reference [3-14] assumes an organic phase of TBP (without any HPT) in contact with 13.6 M HNO₃, containing 64.2 wt% TBP, 32.5 wt% HNO₃, and 3.3 wt% H₂O, on top of an aqueous nitric acid phase containing 67 wt% HNO₃.

The calculation performed in Reference [3-12] is approximately as follows:

TBP concentration in solution = 64.2 % by weight
 TBP molecular weight = 266.32 gms/mol
 Solution density = 1045 gms/L

Weight of TBP in 1 kg of solution = 1000 gms * 0.642 gms/gms of soln
 = 642 gms

Moles of TBP in 1 kg of solution = 642 gms / (266.32 gms/mole)
 = 2.41 mols in 1 kg of solution

For an open system the heat of reaction = 237 kcal/mol of TBP

Total heat generated in the above solution is, therefore

= 237 kcal/mol * 2.41 mols/kg of soln
 = 571 kcal/kg of solution

With heat of vaporization for water at 540 kcal/kg, the amount of water required to dissipate the heat of reaction is = 571 kcal/L / (540 Kcal/kg of water)

Or, amount of water ≈ 1.06 kg of water per kg of above solution

This appears to be the basis of the criterion mentioned in the ISA Summary that an approximate 1:1 mass ratio of water to TBP will provide effective evaporative cooling and prevent a runaway reaction in a nitric acid-TBP system. The criterion is stated as being conservative, since it is based on a TBP-nitric acid system alone, not the 70% HPT-30% TBP in contact with nitric acid that will be used at MFFF.

For a closed system, Reference [3-14] cites data of Nichols corrected by Los Alamos National Laboratory to obtain a heat generation of about 312 kcal/mol TBP for experiments carried out at 120 C. Following the above calculation procedure for the higher heat of reaction, 312 kcal/mol of TBP versus 237 kcal/mole of TBP yields a mass ratio of water to TBP of around 1.3:1.

It is acknowledged that evaporative cooling will not be significant in a closed system because once the system reaches equilibrium further evaporation of water will be prevented and it will cease to be a means of removing the heat generated by the oxidation reaction.

To determine the criteria for the safe venting of red oil, runaway reactions conditions more severe than normally encountered in the process were deliberately created in the Paddleford-Fauske experiments to induce the exothermic reaction. The goal was to establish the required vent size for a given quantity of organics and maximum allowed pressure in the container. The importance of their work is that it gave the industry a simple design criterion of about 32 kg/cm^2 for the threshold amount of organic material needed to initiate a runaway reaction to establish an adequate vent size. Their experiments also clearly determined that the vent size in the Tomsk event was inadequate, about 70% of what was required.

The total amount of organics that is present in any area of concern is a key factor. During normal operation, the amount of organics is expected to be little more than their solubility and the solubility of organics in weak acid is low. It is difficult to estimate during design or early operations the amount of organics that will be carried through in off-normal events. Some scenarios may predict levels that are an order of magnitude higher than normal. Thus, in essence, even if the vent size is suitably designed based on the above Fauske criterion, the amount of TBP/ HNO_3 that is actually present if an accident scenario occurs could be unknown and the amount of safety margin that is available, beyond the criterion for safe venting, will become an important factor from a risk standpoint. The controls that MFFF has established on preventing TBP from migrating to vessels it is not supposed to enter have significantly alleviated this concern (see Chapter 4).

In addition, as Paddleford and Fauske [3-12] point out in their review of the Tomsk-7 event, the vent route must be clear and should not impose any back pressure on the system. The back pressure, as reported elsewhere, may in fact increase the energetics by increasing the solubility of some of the reactive gases in the liquid and, therefore, speed up the reaction.

3.3 References

- 3-1. U.S. Defense Nuclear Facilities Safety Board, "Control of Red Oil Explosions in Defense Nuclear Facilities," DNFSB/TECH-33, November 2003.
- 3-2. International Atomic Energy Agency, "The Radiological Accident in the Reprocessing Plant at Tomsk," STI/PUB/1060, 1998.
- 3-3. J.W. Carrigan, "A Report on a UNH Boildown Evaporator Explosion at Port Hope's Uranium Refinery," July 16, 1980 (cited in Hyder, Reference [3-5]).
- 3-4. M. Benedict, T.H. Pigford, and H.W. Levi, "Nuclear Chemical Engineering," Second Edition, McGraw-Hill Book Company, New York, 1981, p. 512. "At Oak Ridge in 1959, an explosion occurred in a radiochemical plant evaporator that was concentrating a nitric acid solution of plutonium nitrate possibly contaminated by TBP, diluents, and their radiation degradation products."
- 3-5. M.L. Hyder, "Safe Conditions for Contacting Nitric Acid or Nitrates with Tri-N-Butyl Phosphate (TBP)," Westinghouse Savannah River Company, WSRC-TR-94-059, 1994.

- 3-6. U.S. Nuclear Regulatory Commission, "Final Safety Evaluation Report on the Construction Authorization Request for the MFFF at the Savannah Rive Site, South Carolina," NUREG-1821, March 2005.
- 3-7. Shaw Areva MOX Services, "Integrated Safety Analysis Summary," December 17, 2007.
- 3-8. S. Eisenhower et al., Los Alamos National Laboratory, Appendix B to the "Tomsk Report: An Interim Report on Modeling of the Tomsk Incident," to be published in USDOE; cited in Hyder, op cit.
- 3-9. G.S. Nichols, "Decomposition of the Tributyl Phosphate – Nitrate Complexes," DP-526, November 1960; cited in Hyder, op cit.
- 3-10. R.H. Perry, Chemical Engineers Handbook, 6th Ed., p. 3-126, McGraw-Hill, New York, 1984.
- 3-11. E.R. Nazin, G.M. Zachinyaev, and G.F. Egorov, "Thermochemical Oxidation of Components of Extraction Solutions and Boundary conditions of Thermal Explosion: Thermal Stability of Two-Phase Systems TBP-HNO₃ and TBP-Dodecane-HNO₃ in Sealed Vessels," Radiochemistry, Vol. 14, No. 1, pp. 54-57, 2004.
- 3-12. D.F. Paddleford and H.K. Fauske, "Safe Venting of "Red Oil" Runaway Reactions (U)," Westinghouse Savannah River Company, WSRC-TR-94-0649, December 21, 1994.
- 3-13. Shaw Areva MOX Services, "Chemical and Radiolytic Heat Generation in Pre-Autocatalytic Tributyl Phosphate Solutions," DCS01 RRJ DS CAL H 35362.
- 3-14. Shaw Areva MOX Services. "Evaporative Cooling for TBP Nitric Acid Systems," DCS01-RRJ-DS-CAL-H-35614.

4. RED OIL SAFETY STRATEGY IN THE CAR AND THE LICENSE APPLICATION

The MFFF LA [4-1] points out that the Integrated Safety Analysis (ISA) has been a "developmental process." The process started with the safety assessment (SA) phase that was carried out in support of the Construction Authorization Request (CAR) [4-2]; and it became progressively more detailed to support the LA and the ISA Summary [4-3]. The ISA analyzes hazards and potential accident sequences, and identifies the Items Relied Upon for Safety (IROFS) and management measures as well as codes and standards and quality assurance to ensure that IROFS are available and reliable to perform their function when needed. The ISA is designed to be a systematic analysis to identify plant internal and external hazards and their potential for initiating event sequences; the potential event sequences; their likelihood and consequences; and the structures, systems, and components (SSCs) and activities of personnel that are relied on for safety (i.e., IROFS).

4.1 CAR Safety Strategy for Red Oil

As indicated in the LA, the SA of the Design Basis was the first step in the development of the ISA. The SA was completed, and the principal SSCs were identified in the CAR. The process included a hazard assessment and a preliminary accident analysis. The hazard assessment included the identification of specific hazards and the evaluation of those hazards through the development of event scenarios. The preliminary accident analysis consisted of further analyzing events identified in the hazard assessment, assessing the radiological and chemical consequences, establishing a safety strategy, defining the principal SSCs (including administrative controls and their associated design basis), and providing a basis for the selection of those principal SSCs.

Regarding red oil events, the SA in the CAR identified three main safety functions of the principal SSCs:

1. Provide means to ensure that the rate of energy generation from the exothermic nitration-oxidation (red oil) reactions did not exceed the rate of heat removal;
2. Limit the exposure time of organic material such as TBP to the oxidizers, such as nitric acid and the (radiological) metal impurities to reduce the likelihood of a temperature rise that may cause a red oil event;
3. For closed systems, ensure an adequate aqueous phase inventory to provide evaporative cooling to limit temperature rise and maintain temperature below the level for runaway reaction.

The principal SSCs identified in the CAR to accomplish the above safety functions were as follows:

1. Offgas treatment system. The function of this system was to prevent overpressurization by providing an adequate vent capacity in the event of a ROE so the consequences would be tolerable in terms of protecting the worker, the public, and the environment in terms of the performance criteria of 10 CFR 70.61. In the CAR, the provision of adequate venting was analyzed separately for an

open system and a closed system. In the open system, adequate vent area was based on the empirical correlation established by Fauske in terms of the threshold quantity of organic material per unit vent area, i.e., 32 kg of organics per square centimeter, which would allow the gases evolved in the reaction to be safely vented. The CAR design basis value was a vent size based on an organics limit of 12.5 kg/cm²; this provided a safety margin factor of approximately 2.5. In a closed system, when significant amounts of organic material are expected to be present, the offgas system was designed to provide an exhaust path for evaporative cooling of the aqueous phase in any process vessel where a ROE could conceivably occur. The design basis chosen for evaporative cooling was that the heat removed must be 1.2 times the sum of the steam energy input at 133°C (271.4°F) and the energy generated chemically from the reaction.

2. Process Safety Control Subsystem (PSCS): The PSCS was meant to ensure an adequate aqueous phase inventory through continuous feed or injection so that evaporative cooling can be provided in a closed system. The functions of the PSCS were three-fold: first, to limit the bulk temperature of solutions that have degraded organic material; second, to limit the residence time of organics in the presence of concentrated nitric acid; and third, to provide sufficient aqueous phase inventory to ensure evaporative cooling, thus limiting both the bulk temperature of the solution and its ramp rate. While the design identified the controls on the steam temperature used to heat the process vessels, i.e., the first safety function, the other two functions, viz., limiting residence time and providing sufficient aqueous inventory, were expected to be identified in the ISA summary that would be submitted later by the applicant.
3. Chemical Safety Control: This was a quality control meant to ensure that the diluent HPT did not contain any contaminants like cyclic chain hydrocarbons that could initiate a ROE at a lower temperature.

The U.S. NRC's SER providing a review of the CAR is documented in NUREG-1821 [4-4]. In its discussion of red oil phenomena, this report noted that the "applicant indicated that solvent carryover can be considered as an anticipated event in the facility." NUREG-1821 also pointed out that "Duke, Cogema, Stone & Webster (DCS) [4-5] has committed to further evaluate the red oil phenomena, including continuing analyses and experiments which could result in an increase or decrease of the temperature at which action is required to remain below the design basis value. DCS is also evaluating the effect of impurities on the initiation temperature in closed systems." The NRC staff concluded that "operational concerns related to...possible abnormal conditions are best addressed in the ISA when more specific design information is expected to be available."

4.2 Post-CAR Red Oil Safety Strategy

As indicated above, the red oil safety strategy at the CAR stage was mainly mitigative; it was assumed in the design that the organic solvent could migrate to a process vessel where it could potentially encounter the conditions for a ROE. The safety strategy adopted was to ensure that adequate aqueous inventory and vent area would always be

available, even in a so-called closed system, to avoid initiation of a runaway nitration-oxidation reaction.

This approach to ROEs has changed significantly in the post-CAR licensing application stage. The strategy now being proposed is largely preventive, based on attempting to ensure that the organic solvent will not migrate downstream, beyond its solubility limits, into process vessels where conditions for ROEs potentially exist. A presentation made by MOX Services to the BNL team on June 3, 2008 [4-6] indicated several reasons for the change in safety strategy:

1. Evaporative cooling was claimed to have been demonstrated in laboratory scale experiments, based on the ability of aqueous solution to migrate through the organic phase and evaporate at a rate commensurate with heat generation while removing the heat of reaction. However, it was difficult to experimentally demonstrate the effectiveness of evaporative cooling in a full-scale evaporator filled with solvent in the presence of highly concentrated (13.6 M) nitric acid. This would have required either a credible large extrapolation of laboratory-scale data to full-scale conditions or would have involved performing a full-scale experiment that was judged to not be feasible.
2. The aqueous phase injection mitigative system needed to provide continuous aqueous feed to process vessels filled with solvent under both normal and upset conditions as well as the temperature controls needed to demonstrate success were judged to be too complex and difficult to implement.

Accordingly, the safety strategy to reduce risk of ROEs has been changed to focus mainly on prevention and consists of three elements:

1. **Solvent Prevention:** Segregation of separate phase organic solvent (TBP) from acid-bearing and heated process equipment, such as acid evaporators, through process sampling, density monitoring and control, etc., to ensure that TBP does not migrate to unintended process units beyond its solubility limit. IROFS are credited for the success of this strategy and include sampling points and drip trays, process density control loops, and a slab settler. To ensure proper sample head, process sampling is performed with active controls that include redundant air operated valves (AOVs) on lines from the sample tank with redundant controller interlocks and hand switches to prevent unauthorized transfers and programmable logic controllers in the sampling unit and the sampling pneumatic system.
2. **Heat Transfer Strategy:** Meant to demonstrate adequate heat transfer to the external environment of any heat produced from an exothermic reaction using simple convective and radiative heat transfer mechanisms. It is applicable to all vessels *normally* containing separate phase TBP and is designed to ensure that heat dissipated is greater than heat generated through solvent-nitric acid reaction, including catalytic effect of metal impurities like Pu, U, and Zr, and the decay heat from Pu and Am. A computational heat transfer model, which depends on vessel geometry and ambient cell/room temperatures, has been created to evaluate this strategy. IROFS credited for the success of this strategy include geometry of process vessels, temperature control loops to limit self-heating, adequate off-gas venting to relieve pressure from released gases, and

reagent sampling controls to ensure that the proper diluent is added to the process.

3. **Evaporative Cooling Strategy:** Provides for heat removal via evaporative aqueous phase cooling mechanism based on maintaining a minimum quantity of aqueous phase in process vessels where some (limited) amount of TBP could also be present. The success of this strategy is premised on the large heat of vaporization associated with the aqueous phase and assumes the control of key parameters like maintaining minimum water to TBP mass ratio, a maximum TBP layer depth, a maximum process solution temperature and a vented "open" system. IROFS credited include process sampling and administrative flushing controls to limit TBP accumulation in vessels, level controls to maintain minimum aqueous to organic mass ratio, temperature controls to limit solution temperatures, and offgas venting to relieve pressure from released gases.

4.3 Discussion of Red Oil Coping Strategies in the ISA

As indicated in Chapter 3 above, TBP is used at MFFF as a plutonium extractant in the Purification Cycle (KPA) unit. TBP is diluted to 30% by volume in HPT to form the solvent that is used in the aqueous polishing (AP) process. TBP and HPT are both flammable and there are possible explosion events that are associated with the flammability hazards of the solvent. The red oil event is a subpart of the broader hazard of explosion events. It is focused specifically on the exothermic reactions of TBP and its degradation products, including, possibly, products formed by radiolytic dissociation of organic materials, with nitric acid that could lead to explosions.

The ISA states that some probability of a red oil event exists in the following AP process units:

- Purification Cycle (KPA),
- Solvent Recovery (KPB),
- Acid Recovery (KPC),
- Oxalic Precipitation and Oxidation (KCA),
- Oxalic Mother Liquor Recovery (KCD),
- Aqueous Waste Reception (KWD),
- Solvent Waste Reception (KWS),
- Laboratory Liquid Waste Receipt (LGF).

These process units could contain TBP, or its associated byproducts, in addition to concentrated nitric acid, and they are also potentially subject to elevated temperatures. In addition, the solutions in the process vessels contain radioactive materials such as plutonium and americium and are thus subject to radiolysis.

Assuming its occurrence, the unmitigated consequences of the TBP-Nitrate (Red Oil) explosion scenario are high to the facility worker, site worker, and individual located outside the controlled area boundary, so the event must be rendered highly unlikely to conform to the performance requirements of 10 CFR 70.61.

As indicated above, the current safety strategy delineated in the ISA Summary for the red oil event involves the implementation of one of the following approaches, based on the operational constraints associated with each process vessel:

- TBP prevention – segregation of separate phase TBP from acid-bearing process equipment to prevent runaway TBP-nitric acid reactions
- Heat transfer – adequate heat transfer from TBP-bearing vessels to the surroundings to prevent runaway TBP-nitric acid reactions
- Evaporative cooling – maintenance of an aqueous phase in TBP-bearing vessels to ensure evaporative cooling to prevent runaway TBP-nitric acid reactions.

4.3.1 IROFS

The ISA Summary defines IROFS classifications and the risk reduction level attributed to that particular IROFS as follows:

- Active Engineered Controls (AEC) are physical devices that use active sensors, electrical components, or moving parts to maintain safe process conditions without any required human action.
- Passive Engineered Controls (PEC) are devices that do not employ active components, i.e., they use only fixed physical design features to maintain safe process conditions without any required human action.
- Enhanced Administrative Controls (EAC) refer to procedurally required or prohibited human actions, combined with a physical device that alerts the operator that the action is needed to maintain safe process conditions. EAC also include augmented administrative controls that add assurance that the required human performance will be carried out when needed.

The qualitative risk reduction benefits to be ascribed to these different items are discussed in Chapter 5 and Appendix A of the MFFF Standard Review Plan, NUREG-1718 [4-7].

The IROFS selected to implement the safety strategy for the red oil event are described in the ISA Summary. Tables 4-1 and 4-2 are based on the information contained in Tables 5.3.6.2 and 5.3.6.3 of the ISA Summary and describe in detail each of the engineered IROFS and the administrative IROFS, the process units they refer to, the functions they are designed to perform, and the safety strategy that is applicable.

4.3.2 IROFS for TBP Prevention Strategy

The IROFS for the TBP Prevention Strategy consist of: (1) density controls for the detection of HPT/TBP, (2) the slab settler in the KPA unit, (3) process vessels and pipes that ensure no leakage into process cells, (4) administrative control of process sampling, (5) administrative control of drip tray sampling, and (6) administrative controls to preload the slab settler.

Table 4-1. List of engineered IROFS for the red oil safety strategy.

Control	Process Unit(s)	Function	Safety Strategy
Density controls for HPT/TBP detection	KPC, KPA, KPB	Prevent introduction of solvent into equipment which can operate at temperatures above the safety limit	TBP Prevention
		Prevent aqueous organic interface on the KPA slab settler from dropping below the weir	TBP Prevention
		Ensure any separate phase TBP that accumulates in the KPB alkaline waste tank is detected to preclude transfer to the KWD alkaline waste tank	TBP Prevention
		Prevent introduction of HPT downstream of the KPC buffer tank to maintain the safety basis max TBP layer depth at 34 cm	Evaporative Cooling
Process level controls	KPC	Ensures that the minimum water-to-TBP mass ratio of 1:1 is maintained	Evaporative Cooling
Process temperature controls	KPC, KPA, KCA	Ensures that heat transfer from applicable vessels is adequate to avoid self-heating from TBP/nitric acid reactions	Heat Transfer
		Ensures heat input from external sources (e.g., hot water) remains within limits assumed in analysis	Evaporative Cooling
		Ensures solvent temperatures are limited to below lower flammable limit (LFL)	Provides additional safety margin for red oil events
Process vessels	KCA, KPA, KCD, KPB, KPC	Maintains geometry for adequate heat transfer	Heat Transfer
		Designed to make leaks into process cells unlikely	TBP Prevention
Process Vessel Off-gas venting	KCA, KCD, KPA, KPB, KPC, KWD	Ensures that heat transfer due to evaporation remains effective by carrying aqueous phase vapor out of the vessel head space	Evaporative Cooling (KPC unit)
		Ensures that off-gas from TBP nitric acid reactions are adequately vented to prevent overpressurization	Heat transfer (all process units)
Slab Settler	KPA	Passive engineered safeguard to limit the amount of diluent/TBP transferred to downstream vessels by providing sufficient settling time to allow for separation of diluent/TBP from aqueous solution caused by density differences	TBP Prevention
Vessel vent System	KCA	Provides sufficient capacity to allow venting of off-gasses generated from soluble solvent potentially added to KCA drying-calcination furnace to ensure an overpressurization event is highly unlikely	Protects against all solvent explosions in the furnace including any generated as a result of red oil events

Table 4-2. List of administrative IROFS for the red oil safety strategy.

Control	Process Unit (s)	Function	Safety Strategy
Flushing control	KPC, KWD	Ensures a maximum depth of TBP layer within which sufficient heat transfer due to aqueous phase evaporation is demonstrated to prevent red oil explosions in KPC EV2000 and downstream vessels	Evaporative Cooling
Process level control	KPC, KWD	Ensures that the minimum water-to-TBP mass ratio of 1:1 is maintained	Evaporative Cooling
Process temp control	KPC, KWD, SPS	Ensures that the heat input from external sources (e.g., steam from SPS) remains within the limits assumed by analysis	Evaporative Cooling
Drip Tray sampling control	KPC, KPB, KWD, KCD, KPA	Ensures that a sample is taken to establish the source of the leak and ensure detection of organic prior to using a steam jet	TBP Prevention
Process sampling control	KCA, KPB, KWD, KCD, KPA	Confirms the absence of organics before allowing transfers to vessels that operate at temps above the solvent safety basis temp limit	TBP Prevention
Reagent sampling control	DCS	Samples to confirm HPT diluent with appropriate characteristics is introduced into the process	Heat Transfer and Evaporative Cooling
Settler Preload control	KPA	Ensures that KPA slab settler is filled with aqueous phase before process solution potentially containing organic material is added to prevent sending bulk quantities of organics downstream for potential LFL and red oil issues	TBP Prevention

The objective of the density sampling controls, consisting of density transmitters and controllers, is to ensure that a chosen maximum concentration of soluble TBP is not exceeded prior to transferring solution to vessels where any separate phase TBP is to be prevented. These controls are implemented in the KPA control tank to prevent TBP transfer to the KPC unit, in the KCA batch constitution tanks to prevent TBP from reaching the KCD unit, in the KPB alkaline waste tank to prevent transfer of any separate phase TBP to the KWD unit, and in drip trays located in the KPA, KWG, and KCD units. It is stated that the location of the sampling points and associated administrative IROFS will ensure that the samples are representative of a well-mixed tank or vessel and the sample vial traceability, sampling integrity and communication of results from the laboratory to the control room are preserved. These features of the sampling process, which can be regarded as an AEC supplemented by an administrative control, are designed to make TBP migration leading to a ROE highly unlikely.

The slab settler in the KPA unit is credited as a PEC to prevent separate phase TBP transfer to the KCA unit. Administrative controls are imposed on the operation of the slab settler to ensure that the operators implement pre-load procedures and additional density instrumentation is provided to ensure that it operates as designed. The operation of the slab settler is evaluated in Chapter 5 and its possible failure to perform its function is analyzed in Chapter 6.

In some process vessels where sufficient soluble TBP could accumulate to eventually become a separate phase, administrative flushing controls are imposed to flush out the vessels periodically to ensure that the amount of accumulated TBP remains below a pre-determined limit. Administrative controls are also imposed to sample leaks in drip trays to ensure that organics are not transferred by steam jets. Administrative sampling controls are employed to sample for organics before allowing transfer to vessels that operate above the solvent temperature safety limit.

The controls implementing the TBP prevention strategy can fail due to equipment failures or operator errors, or the formation of emulsions or rag layers in the KPA unit that are subsequently transferred to downstream units. The impact of the failures of these controls on the likelihood of a ROE are analyzed in Chapter 6.

4.3.3 IROFS for Heat Transfer Strategy

The IROFS for the heat transfer strategy consist of (1) geometry control of process vessels and pipes, (2) process temperature controls, (3) process vessel off-gas venting, and (4) administrative control of reagent sampling.

The heat transfer strategy is applied to those vessels where passive cooling to the cell environment in conjunction with temperature controls is sufficient to ensure that the vessel contents do not heat up from chemical reactions taking place in the vessel. The success of this strategy implies that adequate room cooling provided by the facility's HVAC system is available. The ISA Summary indicates there is experimental evidence, even at low temperatures where reaction rates are low, that vessels will heat up if they are adiabatic and there are no means for cooling.

According to the ISA Summary "the heat transfer strategy [is] applied to various process vessels in the KPA, KPB, KWD, KWS, and LGF units."

The IROFS controls used to implement this strategy are as follows: vessel geometry, a PEC, coupled with process temperature control, an AEC. The ISA Summary states that using models of red oil reaction kinetics and energy generation, it was analytically demonstrated that heat transfer to the surroundings from those vessels where the strategy will be employed is sufficient to prevent any runaway red oil reactions. The temperature controls employed are based on preventing solvent explosions, for example from the combustion of the diluent HPT, which has a LFL much lower than the initiating temperature of a red oil event. Implementation of these temperature controls is conservative with respect to the red oil phenomenon and provides an additional margin of safety for preventing ROEs.

The other IROFS used in the heat transfer strategy are process vessel off-gas venting and sampling controls on the diluent to ensure quality.

In vessels that employ the heat transfer strategy for maintaining a proper heat balance, the evolved gases must be vented, even at low reaction rates, to prevent any overpressurization that could in turn raise the temperature and the reaction rate. The ISA Summary indicates that "vessel vent sizing is based on widely recognized criteria for red oil vent sizing", an apparent reference to the criterion established by Fauske for successful venting to prevent runaway reactions. The ISA Summary also states: "vessel vents are PEC with a high degree of reliability. Vessel vents are designed to perform their safety function considering all credible failure modes. Therefore, redundancy is not required."

The heat transfer strategy applies to process vessels at lower temperatures (50°C – 55°C and below) where the heat generated in any TBP-acid reaction can be adequately removed passively by dissipation to the cell environment. The success of this strategy depends mainly on the availability of room cooling, i.e., the proper functioning of the HVAC system of the facility. The failure of the HVAC system has implications for many other potential accidents besides a ROE. Thus failure of the heat transfer strategy has not been investigated in this study as it would have greatly enlarged the scope of the study.

4.3.4 IROFS for Evaporative Cooling Strategy

The IROFS for the evaporative cooling strategy consist of (1) process level controls, (2) process temperature controls, (3) process vessel off-gas venting, (4) density control for the detection of HPT, (5) administrative control of process level, (6) administrative control of process temperature, (7) administrative control of flushing, and (8) administrative control of reagent sampling.

For those vessels or tanks where passive heat transfer is not sufficient to remove the energy from both chemical self-heating and the external heat input needed for processing, the strategy chosen is evaporative cooling. Evaporative cooling assumes that the large latent heat of vaporization of the aqueous (water and nitric acid) phase will be sufficient to remove the heat generated by the chemical reactions involving organics and nitric acid provided, (1) the amount of a separate organic phase overlaying the aqueous phase is limited so as not to impede heat transfer by evaporation, (2) adequate venting capacity is available to remove the vapor and other gases that may be generated, (3) the external heat input is limited and (4) the aqueous mass is replenished to maintain a minimum aqueous-to-TBP mass ratio. If the aqueous inventory is replenished, the maximum temperature that can be reached in the presence of adequate venting and, consequently, the absence of significant backpressure, is the nitric acid-water azeotropic temperature of 122°C (251.6°F) associated with the maximum nitric acid concentration of approximately 68 wt%.

The ISA Summary indicates that "in the absence of HPT, the parameters to be controlled and their associated limits are as follows: minimum water-to-TBP mass ratio of 1:1, maximum TBP layer depth of 34 centimeters (cm), maximum process solution temperature of 122°C (251.6°F), and an open (adequately vented) system. In the presence of 5% HPT, the maximum TBP layer depth is reduced to 26 cm."

It is also pointed out in the ISA that "in the absence of a separate aqueous phase, if the initial solution temperature is limited to a maximum of 80°C (176°F), over 600 minutes

(10 hours) is required before the solution temperature resulting from TBP/nitric acid reactions ramps up exponentially. Injection of an aqueous phase (at ambient temperatures) to fulfill the 1:1 minimum water-to-TBP mass ratio at any time during this interval will quench the reaction and maintain the system within a safe operating regime.”

To control the parameters needed to ensure the success of the evaporative cooling strategy, the density controls used for preventing migration of separate phase TBP to the KPC unit are employed. However, some accumulation of soluble TBP can occur in the first stage evaporator of the KPC unit that can eventually lead to the formation of a separate organic phase on top of the aqueous phase in the evaporator or a transfer of TBP to the concentrates tank in the KPC unit.

By controlling the amount of soluble TBP transferred to the KPC unit below a level of 50 mg/l, the maximum amount that can accumulate based on the process flow rate is about 42 liters of TBP per year. An administrative flushing control is implemented to flush out the vessel every six months to limit the maximum accumulation of TBP to ensure that the minimum aqueous-to-TBP mass ratio is maintained along with the maximum TBP layer depth. The ISA mentions that as part of the evaporative cooling strategy, there is “an administrative control consisting of operator action to periodically flush applicable vessels ensuring a maximum depth of TBP layer, within which sufficient heat transfer due to aqueous phase evaporation is demonstrated” [4-2, page 5.3.6-65]. This should effectively limit the residence time of TBP in process vessels. In terms of limiting residence time in pipes, the ISA [4-2, page 4.7-2] describes the fluid transport system as being “designed to efficiently move fluid with a low head and small flowrates. Systems are laid out so as to minimize fluid traps, dead spots, and other volumes that can not be completely drained (with the exception of seal loops).”

The evaporative cooling strategy also uses process temperature controls, which consist of both AEC and administrative controls to maintain process solution temperatures within the allowable ranges. Level controls are used to shut the KPC unit evaporator if there is a low solution level. There is a further administrative control for the operator to verify solution level when the temperature reaches 80°C (176°F) to ensure the maintenance of the aqueous-to-TBP mass ratio. In the case of a potential red oil event in a vessel, based on the reaction kinetics and heat generation, the temperature controls applied are bounded by those used for protecting against solvent explosion events. Since the temperature limit for solvent explosions is more restrictive than for the prevention of red oil, these controls (detailed in Section 5.3.6.2.6 of the ISA) are conservative and credited for prevention of a red oil event [4-2, page 5.3.6-64].

The offgas system is designed to provide an exhaust path for evaporative cooling of the aqueous phase in any of the process vessels where a ROE may have a potential to occur. The ISA [4-2, page 5.3.6-66] states, “in order to ensure that adequate heat is transferred out of the system via evaporation (evaporative cooling) and the vessels are not overpressurized, appropriately sized off-gas vents are utilized.”

Administrative controls on reagent sampling ensure that the diluent HPT does not contain any contaminants like cyclic chain hydrocarbons that could initiate a ROE at lower temperatures. This is accomplished by checking the flashpoint of the fresh diluent to make sure that it is within acceptable parameters.

According to the ISA Summary, the use of "industry codes and standards" and the "management measures ensure that the selected IROFS are reliable and available upon demand; thus, providing additional assurance that it is highly unlikely to expose the facility worker, site worker, individual located outside the controlled area boundary, or the environment to potentially unacceptable consequences associated with this event".

The controls that implement the evaporative cooling strategy, in terms of the success criteria listed above, can potentially fail due to equipment failures and/or errors on the part of operators to implement administrative controls. The implications of these failures on the likelihood of a ROE are evaluated in Chapter 6 below.

4.3.5 Defense-in-Depth

The ISA Summary also points out that in addition to the IROFS, there are several defense-in-depth features that protect the workers "in the highly unlikely case a red oil explosion" take place. These features include: rigid process vessels and pipes that can withstand a significant amount of energy release, process cell barriers that will contain the explosion within a cell, and ventilation systems with HEPA filters that will prevent exposure of workers to any released radioactive materials.

4.3.6 Normal Process Controls

The ISA Summary indicates that normal process controls that are used to maintain aqueous/organic (A/O) interface levels provide protection against a red oil event. These include controls on the aqueous and organic stream feeds, vessel level controls, properties of the diluent, such as density, that help to separate the aqueous and organic phases, and equipment design, such as the settling zones of the mixer-settlers. In addition, normal process temperature controls on vessels help to reduce the potential challenges to the IROFS process temperature controls and maintain a margin below the applicable safety limits. The normal nitric acid controls also help to maintain nitric acid concentrations below the level where the exothermic reactions may be of concern in leading to a ROE.

4.4 References

- 4-1. Shaw Areva MOX Services, "MOX Fuel Fabrication Facility License Application," December 17, 2007.
- 4-2. Duke Cogema Stone & Webster, "Mixed Oxide Fuel Facility Construction Authorization Request," February 2005.
- 4-3. Shaw Areva MOX Services, "ISA Summary," December 17, 2007.
- 4-4. U.S. Nuclear Regulatory Commission, "Final Safety Evaluation Report on the Construction Authorization Request for the Mixed Oxide Fuel Fabrication Facility at the Savannah River Site, South Carolina," NUREG-1821, March 2005.

- 4-5. DCS (Duke, Cogema, Stone & Webster) was the applicant at the time the CAR was issued. They have since been replaced by Shaw Areva MOX Services.
- 4-6. Shaw Areva MOX Services, presentation to BNL team, June 8, 2008.

DRAFT

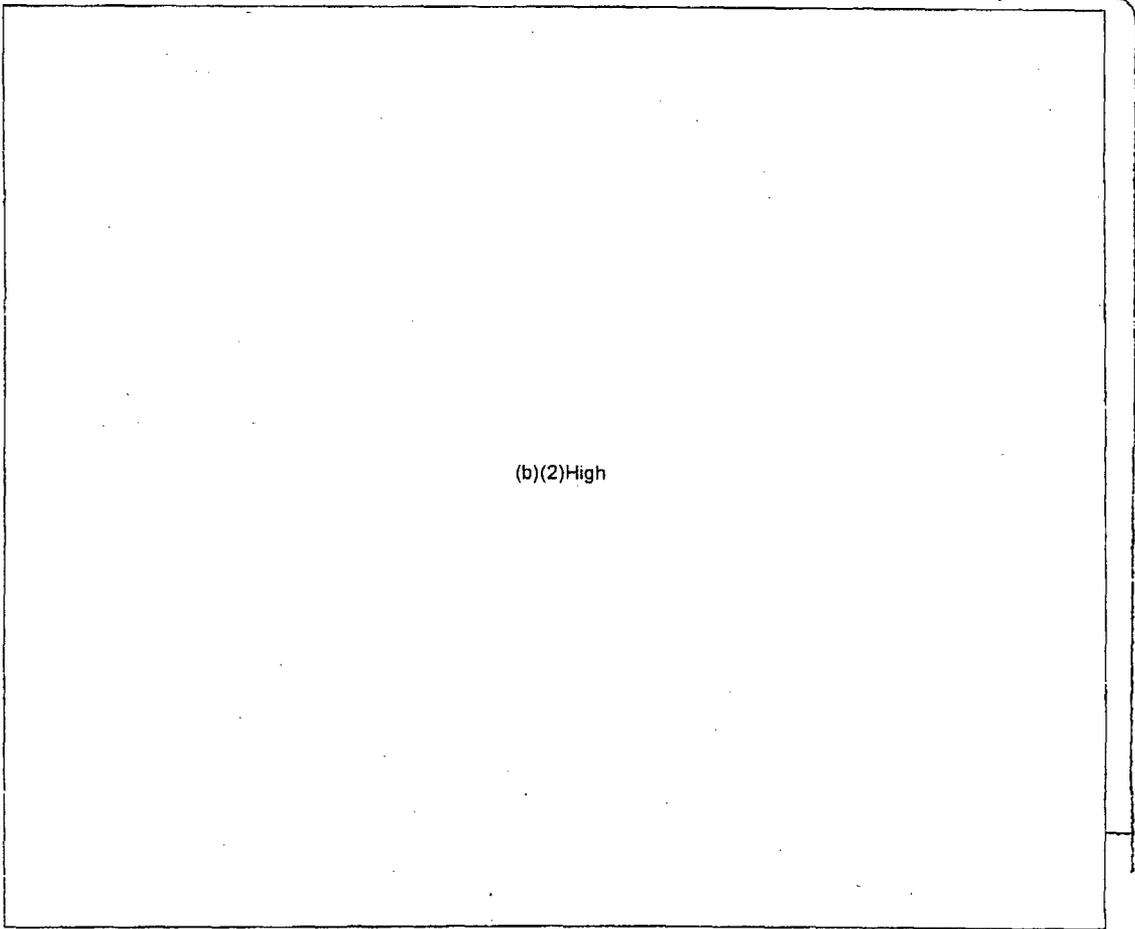
5. MOX FACILITY OPERATIONS RISK RANKING

The MOX facility consists of the following:

- Aqueous Polishing (AP)
- MOX Fuel Fabrication (MP)

The MOX AP process consists of four main areas. They include: (1) Plutonium Purification, (2) Recovery Processes, (3) Waste Storage, and (4) the Offgas Unit.

Figure 5-1 illustrates the AP process units that consist of: (1) the dissolution unit (KDB), (2) the plutonium purification process unit (KPA), (3) the solvent recovery unit (KPB), (4) the oxalic precipitation and oxidation unit (KCA), (5) the oxalic mother liquor recovery unit (KCD), (6) the acid recovery unit (KPC), (7) the offgas treatment unit (KWG), (8) the aqueous waste reception unit (KWD), (9) the solvent waste reception unit (KWS), and (10) the laboratory liquid waste reception unit (LGF). Input and output flows from each of these units are shown in Figure 5-1 that is reproduced in the MFFF LA [5-1].



Ex 2
High

(b)(2)High

5.1 Process Description

Weapons-grade plutonium is received from the proposed pit assembly and conversion facility, and from AFS at the Savannah River site. The plutonium is milled into a powder form and then dissolved in a nitric acid medium with silver as a catalyst to promote dissolution. For the AFS, however, dechlorination is required before dissolution if the chloride content is greater than 500 ppm. According to the ISA Summary [5-2, page 4.2.5-3], the process takes place at temperatures ranging from 20°C (68°F) to 40°C (104°F). Plutonium nitrate is then fed to the purification cycle, where plutonium is extracted through a solvent extraction process, using TBP in an organic diluent HPT, that is, a modified Plutonium Uranium Recovery by Extraction (PUREX) process. The extraction process removes impurities, such as gallium and americium, and the purified plutonium nitrate is fed to a continuous oxalate calcination process that converts it to a plutonium dioxide powder. The oxalic mother liquors produced in the precipitation to oxalate are recycled to the oxalic mother liquor recovery unit. The solvent is regenerated in the KPB unit and the acid is recycled in the KPC unit. The liquid waste storage tanks contain low and high level alpha liquids, stripped uranium and organic waste streams received from various processes in the AP process for temporary storage and pre-treatment before they are ultimately sent offsite for final disposal.

5.2 Generic Risks of Red Oil Excursions

The accident risk space for ROEs can be divided into two parts: the first can be termed a generic risk of ROE due to the occurrence of events, such as internal fires, that can potentially happen in any of the five process units and serve as an external energy source to raise the temperature of acid-organic phases to a level where the autocatalytic reaction can be initiated. For example, as discussed in Chapter 3, the TBP-diluent organic mixture degrades in the presence of water and nitric acid with the rate of degradation dependent on the temperature of the liquid, the nitric acid concentration, and the rates of heat and mass transfer. TBP degrades by hydrolysis to form, successively, dibutyl phosphoric acid, monobutyl phosphoric acid, or phosphoric acid, and butanol.

Butanol has a low flash point of around 40°C (104°F) and a relatively low boiling point (117°C [242.6°F]) and is, therefore, a potential combustible hazard in case of a fire. The degradation rates for TBP increase with temperature and nitric acid concentration and above a certain temperature the degradation, which is exothermic, proceeds at a fast enough rate to generate large amounts of heat and flammable vapor. The heat generated increases the bulk liquid temperature and, therefore, the rate of reaction and can ultimately lead to an autocatalytic reaction.

Generic hazards that can impact the risk of ROE include the following:

1. Internal fires in process cells that may occur due to other than process-related causes;
2. Natural phenomena hazards such as seismic events, external floods, tornadoes, and external man-made sources such as pipeline explosions, etc.
3. Loss of offsite power events, include loss of all AC power, i.e., station blackouts, that can potentially impact the functioning of vital safety systems.

According to the ISA Summary, the applicant has taken measures to render internal fires, due to other than process-related causes, highly unlikely by ensuring that there is either a lack of ignition sources or a very low combustible loading in the AP process cells. The detailed justification is provided in a supporting document [5-3].

External hazards, other than seismic events, are also not a concern at the facility due to their low potential likelihood and the exterior features of the MFFF. The justification for the exclusion is contained in two supporting documents [5-4 and 5-5].

Seismic events have been implicitly treated as a potential cause of process upsets in the analysis that could lead to ROE or other related accident outcomes. The applicant has chosen to apply seismic qualification measures to the IROFS that provide protection to process cells or vessels. For example, all primary confinement boundaries for the KPC acid recovery unit that are identified as IROFS for protection against loss of confinement events are also required to be seismically qualified as are active and passive engineered IROFS that must provide a safety function during a seismic event [5-6].

The basis for the design of the electric power systems in the MFFF is provided in Reference [5-7]. The power system provides for power supply during normal operation, abnormal operation, design basis accident (DBA) conditions, and during loss of offsite power. Normal power is supplied by offsite power sources and consists of two separate and independent sources. The normal power equipment is designed to uniform building code (UBC) earthquake standards. Normal power is augmented by Standby power system consisting of emergency diesel generators also designed to UBC earthquake standards.

If normal power and standby power systems are lost, then the Emergency Power System (EPS), consisting of two redundant, independent emergency diesel generators, provides power to IROFS that need electric power to perform their safety functions. The EPS is designated Class 1E and is qualified under 10 CFR 50 Appendix B QA program for design basis earthquakes, and all normal, off-normal, and accident environmental conditions. The EPS is capable of maintaining full operation of emergency loads for at least 7 days.

Certain IROFS loads are powered from the Uninterruptable Power System (UPS). The UPS will furnish power to designated 120 VAC and 480 VAC important loads. It is stated that the UPS may be either battery or mechanical storage type. The UPS will comply with IEEE 446 and will be designated Class 1E or standby type depending on load served. The UPS comprises of two essential inverter sets. The first inverter set provides power to loads like fire detection, fire control, criticality accident alarms, health physics monitoring, and communication systems. The first essential set will be capable of supplying power for at least 60 minutes. The second inverter set supplies only loads designated as IROFS. It will also be capable of supplying power for at least 60 minutes. It will also supply power to loads such as stack release monitors, seismic detectors, and IROFS HVAC instrumentation. The HVAC equipment providing heating/cooling to the UPS battery room is designated as an IROFS.

Based on this description of the power systems at the MFFF, a station blackout event is likely to have a low frequency of occurrence.

While the generic risks initiated by events like internal fires or external hazards, such as seismic events, have the potential to eventually lead to a ROE, they have not been analyzed specifically in this study for two reasons. First, according to the ISA Summary, the licensee has taken a large number of steps and actions through measures, such as IROFS, to reduce the likelihood of fires as well as the likelihood of externally initiated event sequences to low values consistent with the highly unlikely category of event frequencies. Second, ROEs are only a small subset of the outcomes of generically initiated event sequences; hence, a consideration of generic initiators would greatly enlarge the scope of the study, which is limited to ROE alone during normal facility operation.

5.3 Unit Operation Risks

There are eight process units within the AP process where organics and nitric acid either contact each other during normal operation or have the potential to come into contact. These are: (1) KPA, (2) KPB, (3) KCA, (4) KCD, (5) KPC, (6) KWD, (7) KWS, and (8) LGF.

These eight units are potential candidates where ROEs can occur; the current study has focused on units (1) through (5) since the process conditions there place them at a somewhat higher risk of a ROE compared to units (6) through (8). Recalling the necessary conditions for the initiation of the autocatalytic oxidation (ROE) reaction, each of the five process units is reviewed below in terms of the equipment it employs, the sequence of operations, and the conditions under which the operations occur.

5.3.1 Purification Cycle - KPA

In the purification cycle, plutonium nitrate from the KDB unit is received and the plutonium is solvent extracted and scrubbed for impurities. The inputs to this unit shown in Figure 5-2 are as follows:

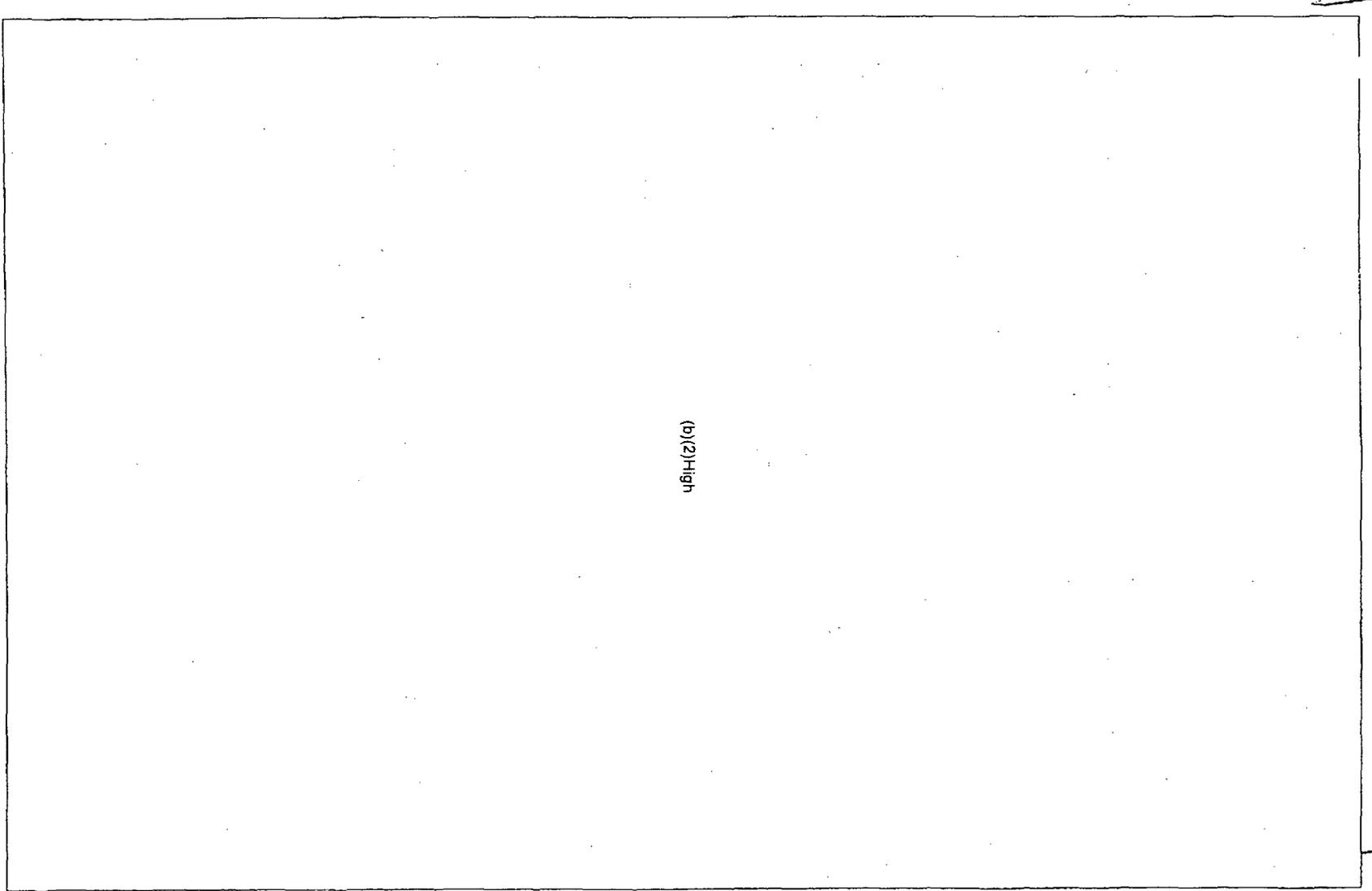
- plutonium nitrate solution from the dechlorination and KDB units
- plutonium nitrate solution recycled from the oxalic mother liquor recovery unit
- high plutonium content solutions from laboratories

The outputs of this unit shown in Figure 5-2 are:

- raffinates (solvent lean, residual feed solution with one or more components extracted) to acid recovery unit (transferred in batches)
- solvent/diluent to solvent recovery cycle (continuous transfer)
- stripped uranium solutions to aqueous liquid waste reception unit (batch transfer)
- purified plutonium to oxalic precipitation and oxidation unit (batch transfer)

Plutonium nitrate solution from Dechlorination/KDB units is batch fed to feed tank TK1000.

~~Official Use Only~~



Ex. 2
High

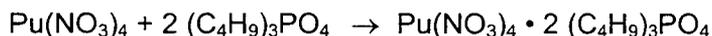
(b)(2)-High

~~Official Use Only~~

PULS 2000

Pu (IV) in 4.5N HNO₃ aqueous solution is extracted by solvent (30% TBP in HPT) in pulsed extraction column PULS 2000 which is the primary extractor that transfers plutonium and uranium to the organic TBP phase leaving the impurities and nitric acid in the aqueous raffinate.

The chemistry of the process described is represented by the equation below:



The Pu (IV) nitrate/TBP complex formed has very low solubility in aqueous solutions of moderate strength HNO₃. The extraction coefficient for Pu (IV) in TBP is a function of nitric acid concentration and temperature. The operating conditions for high extraction efficiency are described in the LA [5-1, page 11.2.6-4] as being a nitric acid concentration = 4.5N HNO₃ and temperature of T= 30°C (86°F).

The flow rates, temperature, nitric acid concentration and pressure of the extraction process are as follows:

The organic phase to the aqueous phase flow ratio is 0.8. [5-1, page 11.2.6-4]

- Temperature: Ambient
- Pressure: Atmospheric
- Nitric acid concentration: 4.5 Normal (ca. 24.5 wt %)

Pressure relief is provided by venting to the scrubbing system. There is very little external energy addition or removal to the process. The pulsation generator provides very low energy input per mass and there is no heating or cooling.

Input and output flow control:

- Aqueous phase in: By airlift under flow control
- Organic phase in: Under flow control
- Aqueous phase out: By airlift under level (interface) control
- Organic phase out: By airlift from overflow

Because of relatively low temperature (ambient), the rate of red oil formation is expected to be low.

However, PULS 2000 is the first potential source contributing to either having organics in the aqueous phase or nitric acid in the TBP phase. Events that may cause a contribution to red oil formation in downstream equipment are listed below:

- Incomplete separation
 - Emulsion formation
 - Smaller droplets

- Wider droplet size distribution
- Inadequate coalescence
- Extraction of HNO_3 in TBP (Depends on solubility and partition coefficient)
- Flooding
- Restriction in outlet flow or airlift failure
- Reduction in density difference (due to lower diluent concentration or lower acid concentration)
- Formation of a third phase
- Formation of a significant rag layer
- Interface detection instrument failure

Following extraction, the aqueous raffinates are washed by diluent HPT in the pulsed scrubbing column PULS 2100 (to remove traces of TBP) and, after complexation of fluorides by a zirconium nitrate solution, transferred to raffinate reception tank TK9000. The impurities are further processed in the raffinate stream. The aqueous raffinate stream goes to the acid and waste units for further processing and, ultimately, to DOE for waste processing.

PULS 2100

PULS 2100 is used to remove dissolved TBP and other organics from the aqueous raffinate into the hydrocarbon diluent.

Equipment type: Pulsed liquid-liquid extraction column with trays or packing

Chemical Inventory:

Organic phase: Diluent	0.3 L
Aqueous phase: Nitric acid	15 L

The aqueous phase to the organic phase flow ratio is 50. [5-1, page 11.2.6-5]

Temperature:	Ambient
Pressure:	Atmospheric
Pressure relief:	Vented to scrubbing system
Nitric acid concentration:	3.7 Normal (approximately 21.0 wt%)

There is little external energy addition or removal. The pulsation generator involves very low energy input per mass, and there is negligible heating or cooling.

Input and output flow control:

Aqueous phase in:	By airlift under flow control
Organic phase in:	Under flow control
Aqueous phase out:	By airlift under level (interface) control
Organic phase out:	By airlift from overflow

This equipment is designed to reduce the probability that TBP and other organics, which may be present in the raffinate, will enter the downstream equipment and therefore it reduces the probability of red oil formation. This is accomplished by washing the raffinate with a hydrocarbon diluent and thereby extracting any TBP that may be present in the raffinate from PULS 2000 (see above). The hydrocarbon diluent, HPT in this case, is resistant to nitric acid attack.

The aqueous phase leaving the KPA unit goes to various intermediate tanks before passing to the KPC unit where nitric acid recovery operations are carried out. Under normal operating conditions, the operation of PULS 2100 should be sufficiently effective at removing TBP from the aqueous raffinate to allow the process to function since the TBP detectors (designated IROFS) in the downstream control tank TK 9100 have a sampling detection limit of 50 mg/L. Table 5-1 shows the solubility of TBP at 25 °C (77°F) in aqueous solutions as a function of nitric acid concentration. Under the conditions prevailing in PULS 2100, the solubility of TBP is approximately 0.266g/L. To reduce this below the detection limit of 50 mg/L, implies that the extraction efficiency of TBP extraction in PULS 2100 should be greater than 81%. This is believed to be readily achievable in units of this type.

Table 5-1. Solubility of TBP in Aqueous Nitric Acid Solutions at 25°C (77°F)
(Source: Science and Technology of Tributyl Phosphate [5-8]).

Conc. HNO ₃ , Molarity	Solubility, g TBP/L	Conc. HNO ₃ , Molarity	Solubility, g TBP/L
0.05	0.426	2.78	0.304
0.125	0.484	3.09	0.304
0.166	0.473	3.16	0.266
0.25	0.458	4.01	0.266
0.255	0.426	5.26	0.203
0.307	0.449	6.41	0.178
0.5	0.449	7	0.133
0.522	0.447	8.5	0.133
0.79	0.395	9.61	0.185
0.994	0.427	9.92	0.147
1	0.426	11	0.170
1.11	0.418	12	0.328
1.5	0.391	13.1	0.328
1.97	0.328	13.8	0.666
1.98	0.355	15.6	1.704
2.15	0.355	15.9	1.217

If operated properly, HPT should replace, or at least dilute the organics in the raffinate. However, if a stable emulsion is formed in PULS2000 and carried forward to PULS2100, it is unlikely that pure HPT wash would break the emulsion.

Possibility of Red Oil formation:

This equipment, operating at low temperature and with mostly HPT as the organic phase, is unlikely to contribute to red oil formation. It should be mentioned that while HPT itself is resistant to nitric acid, the impurities present in commercially available HPT might not be as resistant. Quality control of incoming HPT, especially with regard to its bromine number (degree of unsaturation), is crucial. This feature is specifically mentioned in the ISA as a quality assurance item since HPT quality is designated as an IROFS.

Contribution to Red Oil formation in downstream equipment:

This equipment with the diluent as the only organic feed does not increase the probability of red oil formation in downstream equipment.

PULS 2100 Events:

(See list under PULS 2000)

PULS 2200

The loaded solvent stream from PULS 2000 is scrubbed with 1.5 N nitric acid (about 9 wt%) in the pulsed scrubbing column PULS 2200 to remove impurities that may have been co-extracted in the solvent phase. This also helps to reduce the amount of nitric acid dissolved in the TBP phase. The nitric acid in this step contains aluminum nitrate to remove any fluorides.

Equipment type: Pulsed liquid-liquid extraction column with trays or packing

Chemical Inventory:

Organic phase:	TBP and Diluent 11.6 L
Aqueous phase:	Nitric acid 15 L

The aqueous phase to organic phase flow ratio is 0.3. [5-1, page 11.2.6-5]

Temperature: Ambient

Pressure: Atmospheric

Pressure and pressure relief: Vented to scrubbing system

Nitric acid concentration: 1.5 Normal (approximately 9.0 wt% nitric)

External energy addition or removal:

Pulsation generator:	Very low energy input per mass
Heating and cooling:	None

Input and output flow control:

Aqueous phase in:	By airlift under flow control
Organic phase in:	By airlift under flow control
Aqueous phase out:	By airlift under level (interface) control
Organic phase out:	By airlift by overflow

Possible Events:

This equipment reduces the probability that HNO₃ (which may be present in the solvent phase) will enter the downstream equipment and therefore reduces the problems associated with red oil formation. This is accomplished by washing the solvent phase with dilute nitric acid and thereby extracting any dissolved nitric acid that may be present in the solvent from PULS2000 (see above).

Under normal operations, the dilute nitric acid replaces the concentrated acid or at least dilutes the nitric acid in the solvent. If a stable emulsion is formed in PULS 2000 and carried forward to PULS 2200, contact with dilute acid may help break the emulsion due to the difference in pH.

Red oil formation:

Because of relatively low temperature (about 30°C [86°F]) and dilute nitric acid (1.5 N or 9 wt%), the rate of red oil formation is expected to be very low; in fact, lower than in PULS2000.

Contribution to red oil formation in downstream equipment:

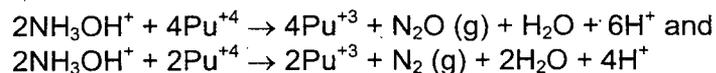
This equipment with the dilute acid as the aqueous feed does not increase probability of red oil formation in downstream equipment.

PULS 2200 Events

(See list under PULS 2000)

PULS 3000

This step of the process performs a valency adjustment. In PULS 3000 Pu(IV) in the solvent phase from PULS 2200 is reduced to Pu(III) with 0.15M HAN (hydroxylamine) solution and then re-extracted in acidic water (0.1N nitric acid or 0.7 wt%). The plutonium stripping (i.e., reduction reactions) by HAN outlined in the LA [5-1, page 11.2.6-25] are:



These reactions are exothermic, and proceed rapidly while the reaction rate increases with temperature and concentration. Both solvent and aqueous phases are first heated to about 65°C (149°F) to accelerate chemical reduction of Pu(IV).

Equipment type: Pulsed liquid-liquid extraction column with trays or packing

Chemical Inventory:

Organic phase: TBP and Diluent = 14 L
Aqueous phase: Nitric acid = 25 L

The organic phase to aqueous phase flow ratio is 1.3 [5-1, page 11.2.6-7].

Temperature: Maintained below 48°C (118.4°F)

Pressure: Atmospheric

Pressure and pressure relief: Vented to scrubbing system

Nitric acid concentration: 0.2 Normal

External energy addition or removal:

Pulsation generator: Very low energy input per mass
Heating and cooling: solvent and acid feeds are heated

Input and output flow control:

Aqueous phase in: By airlift under flow control
Organic phase in: By airlift under flow control
Aqueous phase out: By airlift under level (interface) control
Organic phase out: By airlift by overflow

Possible Events:

The PULS 3000 events are the same as those listed under PULS 2000.

Red oil formation:

Despite the higher operating temperature, the rate of red oil formation is expected to be very low because of the very low concentration of nitric acid (0.2N).

In terms of contribution to red oil formation in downstream equipment, it is possible that the acid phase may transport organics to the downstream equipment due to solvent-acid contact.

The stripped plutonium is washed with diluent in the pulsed scrubbing column PULS 3100 to remove any traces of organic material before the final valence adjustment. Any remaining U in the stripped Pu aqueous phase is separated from Pu by

solvent extraction in the pulsed scrubbing column PULS 3200. For batches with low U content, a bypass of PULS 3200 is available.

Intermediate Tanks (TK9000, TK9500, TK9100, TK1000, TK1500)

It is assumed that, along with the raffinates, some organics are fed to these tanks. In the tanks that are not mixed, the organics will form a separate upper layer unless a stable emulsion is fed to the tank, in which case there will be a single emulsion phase along with a bulk phase. Location of the emulsion in the tank will depend on its composition and, therefore, its apparent density.

The MFFF process relies heavily on tank mixing in application of its IROFS. Tanks need to be well-mixed in order to effectively apply the heat transfer strategy, as well as perform representative sampling of the tanks' contents. If the vessels are not well-mixed, then hot spots or uneven heat distribution can occur. Similarly, a sample taken from an unmixed tank can imply that there is little or no TBP present, even if that isn't actually the case.

Feed Tank KPA TK1000 is geometrically safe and its contents are mixed by a sparging pipe supplied with compressed air [5-2, page 4.2.6-3]. The Raffinates Reception Tank TK9000 is designed to be geometrically safe and is mixed by an air sparger [5-2, page 4.2.6-20]. Control Tank KPA TK9100 is geometrically safe and homogenized with an air sparging pipe [5-2, page 4.2.6-21]. Recycling Tank KPA TK9500 is geometrically safe and homogenized with compressed air from a sparging pipe [5-2, page 4.2.6-22].

Tanks can be fed either continuously or intermittently. The intermittent flows are likely to disturb the separated phases causing the light phase to enter the feed to the evaporator train.

Control Tank KPA TK9100 has IROFS process sampling controls to ensure that maximum concentration of TBP in the solution is sufficiently low (below the sampling limit of 50 mg TBP/L) before its contents are transferred to vessels further downstream. These controls are meant to prevent: (1) a separate phase layer of TBP and (2) greater than 50 mg/L of soluble TBP, from moving to downstream vessels. This assumes that the tank is well-mixed, and therefore any organic phase (lighter layer) will not accumulate in the tank. If the light phase is not removed frequently, then it is possible that a portion of the organics will remain in contact with the acid for a long time. Therefore, despite a low tank temperature and relatively low nitric acid concentration, there could be some red oil formation.

Tanks are at atmospheric pressure and vented to the scrubber system. The only heat removal is through the tank walls to the atmosphere by natural convection. The amount of heat lost to the atmosphere is a function of the liquid level in the tank. The following (qualitative) scenario may be of some concern.

At low liquid level, if there is some exotherm due to the onset of a chemical or radiolysis reaction, the temperature of the tank contents will rise. Essentially only water will evaporate because the aqueous mixture composition is below the azeotrope on the water side. Water evaporation will increase the acid concentration and therefore increase the reaction rate. Additionally, loss of water will decrease both the total mass and the liquid specific heat and thus the temperature rise will be greater for the same

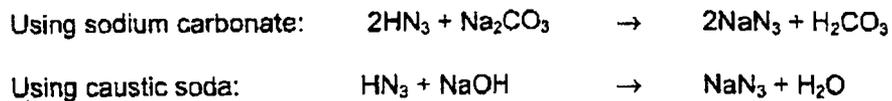
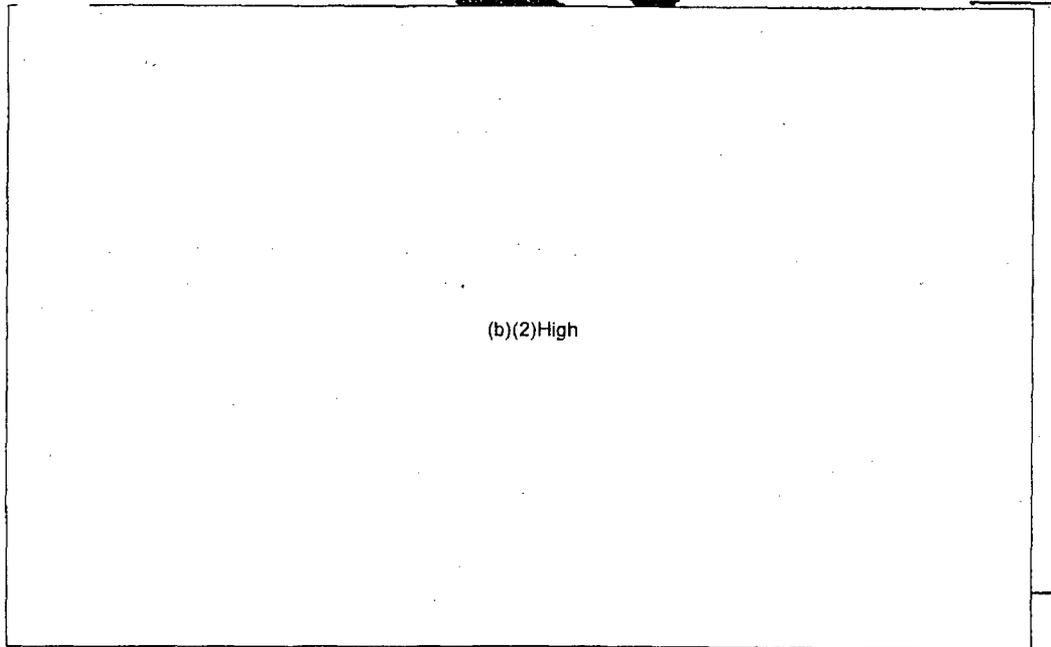
heat generation, further increasing the reaction rate. However, the tanks are provided with temperature sensors that would allow the operator to take corrective action in case of a rise in temperature and terminate any self-heating chemical reaction.

5.3.1.1 Summary of ROE Risk in the KPA Unit

Based on the discussion of each of the operations in this unit, the overall risk of a ROE is judged to be low due to two main factors: either the operations are conducted at relatively low (ambient) temperature or they involve very low nitric acid concentration. However, as outlined in the analysis of events that can occur in the extraction process in PULS 2000, it is possible that this unit can serve to introduce organic material to places it is not intended to go through features that are intrinsic to liquid extraction processes.

5.3.2 **Solvent Recovery Unit**

The solvent recovery cycle operation is schematically depicted in Figure 5-3. The solvent TBP is received from the purification cycle at a temperature of about 50°C (122°F) and undergoes a series of alkali washes to remove TBP degradation products, like DBP and MBP, and hydrazoic acid left over from the HA reactions. A 2-stage sodium carbonate wash at ambient temperature is followed by a 4-stage caustic soda wash to further remove the degradation products. Since hydrazoic acid is soluble in TBP it is necessary to remove it before the solvent is fed back and recycled into the KPA. The chemistry of HN₃ removal is outlined in the [5-1, page 11.2.7-3] as follows:



The DBP and MBP migrate from the organic phase to the aqueous phase after the alkaline wash. The aqueous wastes after washing are subjected to a diluent wash in a mixer-settler battery at ambient temperature to further remove any traces of entrained solvent. The washed solvent is returned to the KPA via a dosing pump. Pure TBP makeup is added as needed to adjust the TBP content of the washed solvent.

5.3.2.1 Summary of ROE Risk in the Solvent Cycle Unit

The risk of a ROE in this unit is judged to be very low mainly due to the alkaline environment in which the operations are performed.

5.3.3 Acid Recovery Unit

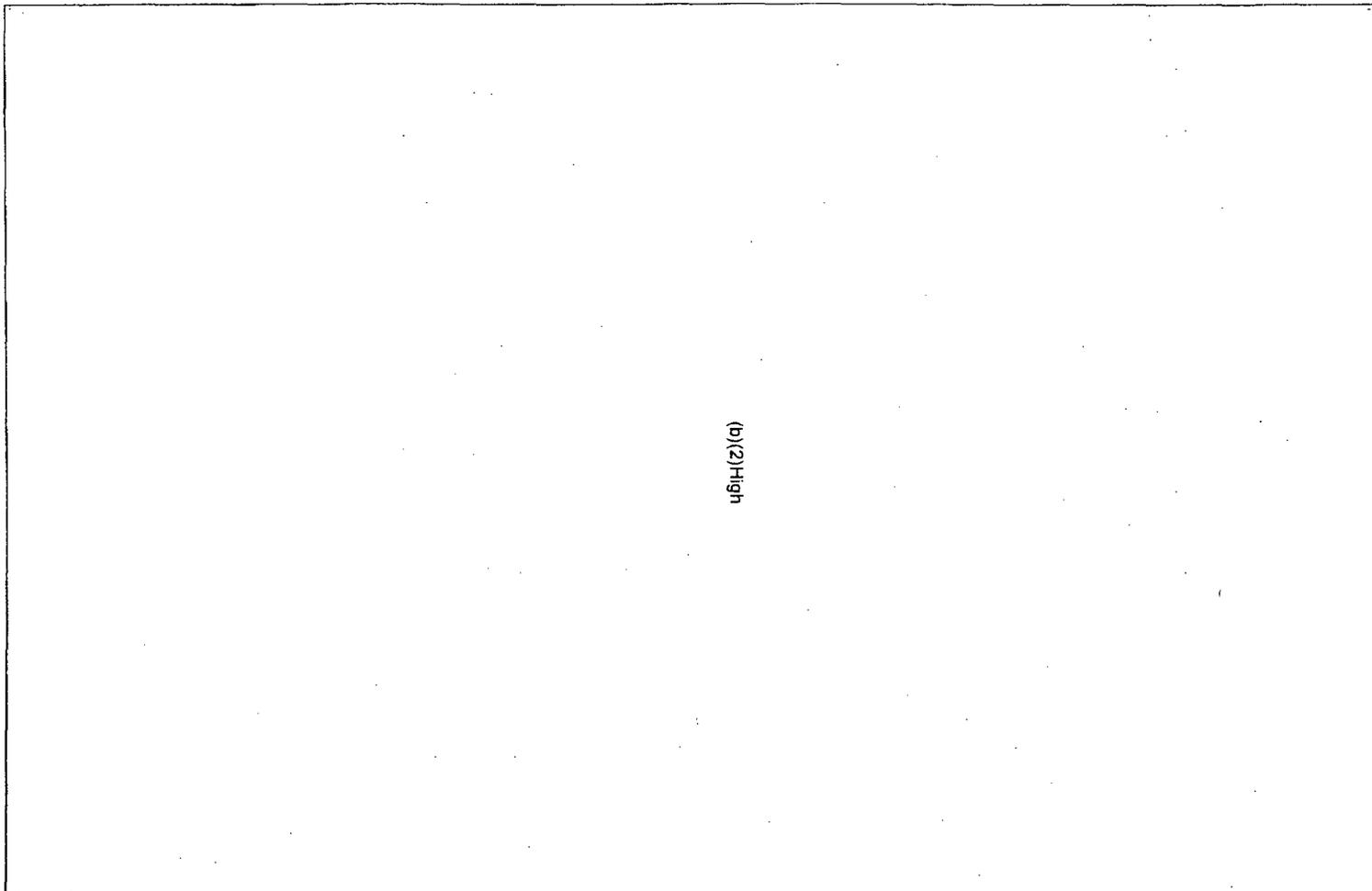
The function of the acid recovery unit shown in Figure 5-4 is to recover concentrated nitric acid for recycling in the overall process, concentrate the radioactivity in the effluents for sending it to the liquid waste unit, and recover the distillates from the rectification column for use in the KWG and KPA units. The acid recovery unit receives the extraction raffinate from the purification cycle, oxalic mother liquor distillates from the KCD, KWD, and KWG units, and effluents from the laboratories in batches. Active liquid effluents are continuously received from the offgas treatment equipment ventilation system.

Red oil formation and decomposition is most likely to occur in the evaporator area because of its higher operating temperature and higher nitric acid concentration. The acid recovery evaporators, EV2000 and EV6000 and the rectification column, CLMN2500 are used to separate nitric acid from contained non-volatile salts and concentrate it to near azeotropic concentration.

The discussion below assumes that, due to various failures of controls discussed further in Chapter 6, a sufficient amount of organics has either entered the evaporator train from the previous unit operations or has accumulated due to administrative failures to flush out the system periodically. Once in the evaporator, whether the organics will form a separate layer or not depends on several factors, including:

- The evaporator design, more specifically the degree of mixing
- The concentration of nitric acid, which affects the degree of solubility of the organic solvent in the aqueous phase (the evaporator temperatures are higher than the previous unit operation and thus the aqueous phase will tend to dissolve a higher amount of organics.)

~~Official Use Only~~



(b)(2)High

Ex 2
High

~~Official Use Only~~

Evaporator EV 2000

This evaporator is fed acidic raffinate, vent scrubber liquid from the offgas treatment unit and waste streams from the laboratory from Feeding Tank, TK1500. It separates volatile acid and water from the insoluble salts. Vapor for the evaporator is condensed and re-evaporated in EV 6000. The bottoms containing acid and non-volatile salts are sent to a waste handling system.

Type: Evaporator body for vapor/liquid separation with external thermosiphon reboilers.

Operating temperature: 65°C (149°F)
 Operating pressure: 100 mmHg absolute
 Heated by: Temperature controlled hot water
 Heat removal by: Water cooled condenser
 Vacuum generation by: Liquid ring vacuum pump

Feed: Continuous
 Distillate removal: Continuous
 Bottoms removal: Intermittent

Areas where conditions necessary for ROE could exist

The bottoms are removed intermittently. The LA [5-1, page 11.2.12-1] states, "Concentrates from the first evaporator are drawn off several times a day at a constant rate by an airlift." It is not clear if the evaporator is completely drained or not. If it is not completely drained, and if there is a top separated organic layer, then the organic layer will continue to accumulate. On the other hand, with thermosiphon reboilers it is not possible to continue operation with a variable (especially low) liquid level.

The feed liquid acid concentration is below its azeotrope. Nitric acid and water form a high boiling azeotrope at about 68 wt% acid (13.5 N), which has a normal boiling point of about 122°C (251°F) at atmospheric pressure and, according to Boulblik [5-3], at about 72°C (161.6°F) at 100 mmHg, the EV 2000 operating pressure. Simple distillation or evaporation can not increase the acid concentration beyond the azeotropic value if the starting material concentration is below the azeotrope. At concentration below the azeotrope during evaporation, the vapor will be rich in water causing acid concentration in the liquid to increase, until it reaches the azeotropic concentration. Once the azeotrope is reached, the vapor and liquid compositions will be identical and thus no further concentration will take place. Until the bottoms are drained, the acid concentration in the liquid will keep rising and approach the azeotrope (68 wt% or 13.5N). This acid concentration is well above the 10N limit recommended in the literature for safe operation. Accident scenarios that may develop from this condition leading to a ROE are analyzed in Chapter 6 using failure modes and effects analysis techniques.

Evaporator EV 6000

Distillate from EV 2000 is re-evaporated in steam heated EV 6000. Vapors from EV 6000 are fed to column CLMN 2500 for acid rectification; bottoms concentrate is intermittently removed and recycled to EV 2000.

Type: Evaporator body for vapor liquid separation with external thermosiphon reboilers.
 Vapors fed to CLMN 2500.

Operating temperature:	120-122°C (248-251.6°F)
Operating pressure:	Near atmospheric ¹
Heated by:	Steam under pressure control
Heat removal by:	Water cooled condenser
Feed:	Continuous
Distillate removal	Continuous
Bottoms removal	Intermittent

Areas where conditions necessary for ROE could exist

EV 6000 has the same areas where conditions necessary for ROE could exist as indicated above for EV 2000. If organics do enter EV 6000, the probability of red oil formation and possible exothermic reactions are higher than in EV 2000 due to the following:

- higher operating temperature, 122°C (251.6°F) versus 65°C (149°F)
- higher acid concentration, near the azeotrope point
- higher heat source temperature (steam versus hot water)
- higher tube wall temperature
- failure of cooling in condenser CND 2000 will increase the reboiler pressure, and therefore the temperature could increase above its normal 122°C (251.6°F)
- Any obstruction to vapor flow in column CLMN 2500 or the vapor line will increase reboiler pressure
- An exothermic reaction in EV 6000 will add to the heat input from steam and may exceed condenser CND 2000 capacity, causing increased back-pressure

However, as discussed later in Chapter 6, the likelihood of the presence of organics in EV 6000 in sufficient quantity to be of concern from a ROE standpoint is significantly lower than in EV 2000. The ISA Summary states that due to the aggressive conditions in EV 6000 and CLMN 2500, the rate of TBP destruction will be faster than the rate of TBP accumulation in these vessels. This is likely to be the case because the amount of TBP that can reach EV 6000 beyond the sampling limit is small and since there is frequent draining of EV 6000, very little is like to accumulate. Further the high operating temperature will destroy the soluble TBP thus significantly decreasing the possibility of a ROE. This is discussed further in Chapter 6 below.

Rectification Column CLMN 2500

Vapors from EV 6000 are rectified in column CLMN 2500. The feed is separated into acid water as distillate and concentrated nitric as the bottoms product.

¹The condenser CND 2800 is vented through a steam ejector to the vent system. Pressure in EV 6000 will be almost the same as the pressure at the condenser (nearly atmospheric).

Type: CLMN 2500 is a trayed distillation column with a water cooled condenser and a steam heated reboiler.

Operating temperature:	120-122°C (248-251.6°F)
Operating pressure:	Near atmospheric (see footnote 6)
Type of Internals:	Multiple Bubble-cap trays
Feed location:	Column middle
Heated by:	Steam under pressure control
Heat removal by:	Water cooled condenser

Feed:	Continuous
Distillate removal	Continuous
Bottoms removal	Continuous

Areas where conditions necessary for ROE could exist

The areas where conditions necessary for ROE could exist for the CLMN 2500 system are same as that noted above for EV 6000.

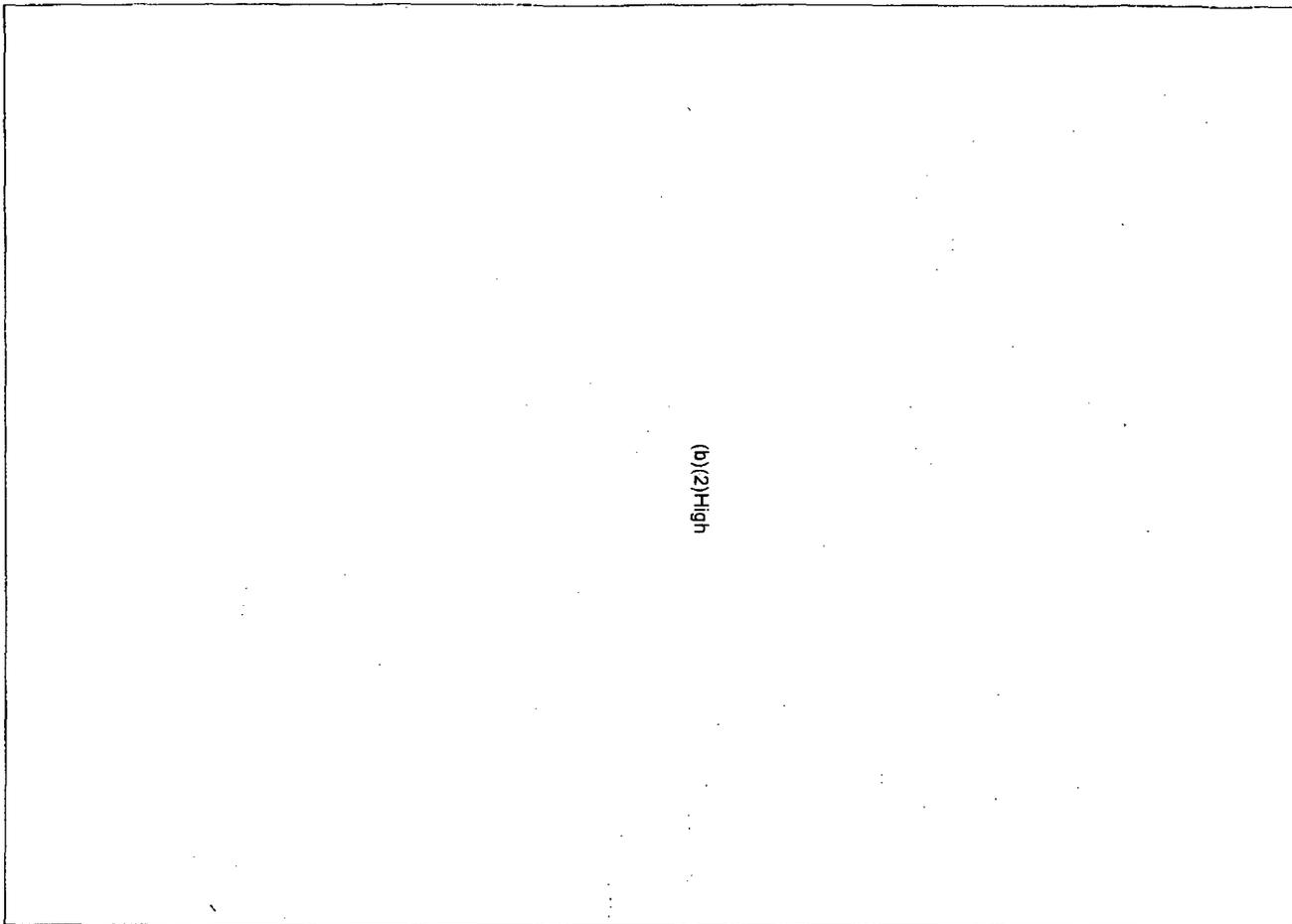
5.3.3.1 Summary of ROE Risk in the KPC Unit

The risk of ROEs in the acid recovery unit is judged to be higher than in the other units. Operation at high temperature and high nitric acid concentration coupled with the feature that the acid recovery unit receives input from a number of different sources increases the likelihood that the essential conditions for a ROE will be fulfilled especially if there is an equipment failure leading to loss of control of some vital parameter like temperature or adequate venting. Chapter 6 contains a quantitative analysis of the probability of a ROE in the acid recovery unit.

5.3.4 Oxalic Mother Liquor Recovery Unit (KCD)

The KCD as shown in Figure 5-5, concentrates oxalic mother liquor received from the KCA. It also receives ventilation effluent droplets from the oxidation and degassing columns. This unit concentrates the oxalic mother liquors in a subcritical evaporator to destroy the oxalic ions and remove the plutonium from the distillates. The distillate which contains nitric acid and water is sent to the KPC as previously discussed. The concentrate is recycled batchwise to the KPA.

~~Official Use Only~~



(b)(2)High

EX 2
High

~~Official Use Only~~

The functions of the oxalic mother liquor recovery unit are:

1. Primary recovery of nitric acid that is then concentrated in the acid recovery unit.
2. Concentrate plutonium in the mother liquid bottoms (Concentrate) so that it is suitable as recycle to the Pu purification section.

The primary production controls for these two streams to be suitably recycled are:

1. Concentrate that is free of oxalate ions, and
2. Distillate that this is free of Pu.

Mother liquor during concentration is treated to relatively high temperature, (about 120°C [248°F]), long residence time, and high nitric acid concentration to assure complete destruction of the oxalate ions.

To obtain distillate free of plutonium, the vapors from the evaporator are thoroughly washed with clean reflux through a series of bubble cap trays and a demister.

Red oil can only become a concern if organics are somehow able to reach this unit. To prevent this from happening, various IROFS controls, including organic phase detection controls and the slab settler, are implemented to prevent separate phase TBP from being transferred downstream. A more detailed discussion of this issue is presented on page 5.3.6-62 of the ISA, where it is stated that, "process sampling controls ensure that the maximum concentration of TBP in solution is satisfied prior to transferring solutions to vessels where TBP (separate phase) is prevented. IROFS process sampling controls are taken from the following vessels to protect downstream units vulnerable to a red oil event: both KCA constitution tanks to protect the KCD unit and KPA control tank to protect the KPC unit." In terms of the sampling procedure, the ISA [5-2, page 5.3.6-63] details, "these sample points and the associated administrative IROFS required to ensure the sample is representative of the contents of the tank (i.e., vessel isolation, vessel homogenization, sample line purging, sample vial traceability, laboratory sampling process, and communication of results from laboratory to the control room) ensure red oil explosions are highly unlikely. However, in case these preventive measures are ineffective for any reason, the principal concerns in this unit can be summarized as follows:

1. The conditions required for destruction of the oxalate ions, namely high nitric concentration, high temperature and long residence time are precisely the same conditions that promote red oil explosion. These conditions exist in this unit operation as *normal* operating conditions.
2. The necessity of obtaining plutonium free distillate introduces a number of complexities to the unit that may make rapid and reliable venting of generated gases difficult.

These risks are discussed below.

The LA (5-1, page 11.2.11-2) provides the following process description:

The oxalic mother liquors, supplied from the feeding tank, are concentrated in the natural-circulation thermosiphon evaporator. The evaporator included the following components:

- A boiler used for evaporation of the feed solution and reflux from the rectification column. It is a tubular exchanger. The heating fluid (steam) occupies the shell side and the mother liquor to be evaporated circulates in the tubes.
- Instrumentation used for measuring the level, density, and temperature.
- A rectification column, which backwashes the steam, rectifies the acid and decontaminates the distillates.

Areas where conditions necessary for ROE could exist

Operating Conditions:

As stated above, the normal operating condition itself will promote a ROE in case a sufficient quantity of organic material is present. Hence reliable and adequate venting per the Fauske criterion or some other acceptable criterion will have to be implemented.

Reboiler Temperature:

The reboiler is heated by a closed circuit steam system that is separate from the plant steam system. This is to prevent possible contamination of the plant system with plutonium for EV 3000. The steam is generated in EV 5000. The normal operating temperature on the process side is 120°C (248°F) (average bulk temperature). The maximum tube wall temperature, however, is higher and is fixed by the maximum steam temperature. The maximum steam temperature in turn is bounded by the maximum steam pressure relief valve setting on the system.

Most steam heating systems in such plants have a few degrees (10-25°C) of superheat, either as a deliberate superheating section in the steam generator (a more expensive option in small steam generators) or as a result of pressure let-down between steam generation point pressure and the use point pressure. This is mostly done to minimize steam losses via condensation in the supply piping. For example, if steam were produced at 10 Bar (atm) (1 MPa) in a standard boiler and used at 4 Bar (atm) (0.4 MPa), the superheat would be a little less than 21°C. What is more important is the amount of heat available from superheat (less than 2 kJ/kg/C) versus that available from condensation (2133 kJ/Kg). Because of high heat release and high condensing heat transfer coefficients (versus convective coefficient for superheated steam), in reboilers and other steam heated equipment the condition known as dry tube wall zone is rare. For practical considerations, the assumption that the tube wall is at the steam saturation temperature at the condensing pressure is reasonable as shown below.

The process control system controls the average process side bulk temperature. The difference between the controlled temperature and the tube-wall temperature T_w is a function of individual heat transfer coefficients and heat load:

$$Q = U \cdot A \cdot (T_s - T_p) = h_s \cdot (T_s - T_w) = h_p \cdot (T_s - T_w)$$

Where,

Q = heat load, kW

A = heat transfer area, M²

U = Overall heat transfer coefficient, kW/M²/°C

h_s = steam side heat transfer coefficient, kW/M²/°C

h_p = process-side heat transfer coefficient, kW/M²/°C

T_w = wall temperature, °C

T_s = steam side bulk temperature, °C

T_p = process side bulk temperature, °C

Ignoring the difference between the tube wall inside and outside temperatures, the above leads to the average tube wall temperature as

$$T_w = (h_s \cdot T_s + h_p \cdot T_p) / (h_p + h_s)$$

Typically, the steam side heat transfer coefficient (5500-6000 kW/M²/°C) is more than an order of magnitude higher than process side heat transfer coefficient (400-600 kW/M²/°C), hence the above tube wall temperature can be simplified to

$$T_w \approx T_s + h_p / h_s \cdot T_p$$

Or, $T_w \approx T_s$

The process side heat-transfer coefficient, h_p, is a function of the state of the tube wall, such as whether it is fouled or clean, and the thermosiphon circulation rate, and its physical material properties. The circulation rate and therefore the fraction of liquid that is vaporized is a strong function of level and, therefore, the optimum level needs to be maintained during operation. As noted above, because the steam side heat transfer coefficient is often about one order of magnitude higher than the process side heat transfer coefficient, the tube wall temperature is almost equal to the steam temperature. In fact, the steam pressure or the equivalent saturated temperature is a reasonably accurate measure of the tube wall temperature.

The above equation indicates that the wall temperature will be higher than the bulk temperature; up to the maximum steam temperature (as Q goes up or as h goes down).

Besides reduction in circulation, the process side heat-transfer coefficient can be substantially reduced as a result of tube fouling which may occur because of the presence of organics, introduction of a rag layer in the reboiler or the presence of solids.

Vent path:

Thorough decontamination of rising vapors requires several cleaning steps. Although bubble cap trays used are effective in cleaning the vapors, they do so by imposing a tortuous vapor path. In the chemical industry there have been numerous recorded incidences where a sudden rise in vapor flow has dislodged tray stacks [5-...]. These can then cause a major obstruction to vapor flow and consequently increase the bottom pressure.

In addition, there is a wire mesh demister above the tray stack. This is susceptible to plugging. It is important that the source pressure, such as at the reboiler vapor return to the evaporator body, is monitored and maintained at a safe level. This is to ensure that the principal assumption of an open system remains valid.

Discharge of the concentrate:

It is not clear in either the LA or the ISA Summary whether the evaporator is completely or only partially emptied during each draw off.

Partial draw-off: If the concentrates are drawn off only partially then any accumulated organic layer, which will float on heavier acid layer, will continue to accumulate in the system. In this case, even a small amount of continuous organics flow to the evaporator could eventually lead to an accumulation of the inventory of organics in the evaporator.

Partial draw-off also causes the level in the evaporator to vary and therefore causes non-optimum reboiler operation and possible increase in tube-wall temperature.

Complete draw-off: Complete de-inventory will prevent any possible accumulation of an organics layer. However it requires unit shut-down and thus a batch operation.

Steam pressure management:

The unit has its own steam generation. Steam for the unit is generated in EV-5000, a closed circuit vaporization system heated with plant steam. The maximum steam pressure is the maximum process temperature limited by steam relief valve set pressure (2.13 bar gage). This corresponds to a 135°C steam condensation temperature.

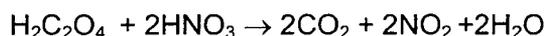
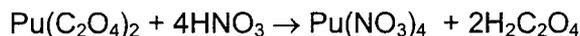
Loss of cooling:

Complete loss of cooling can occur due to cooling system failure. Partial loss of cooling can occur if the column reflux is reduced or stopped. Either loss of cooling scenario will increase bottom (vaporizer) pressure and therefore the temperature; limited by steam temperature stated above.

Evaporator EV 3000

High acidity, high temperature and long residence are used in EV 3000 in order to destroy residual oxalic ions and convert Pu(III) and Pu(IV) to Pu (VI). Section 11.2.1 of the LA describes the process chemistry as follows:

"The residual oxalic acid ion content in the concentrates does not exceed 10^{-3} M. A high level of acidity (approximately 13.6 N and a temperature of around 248°F [120°C] in the evaporator) destroys the oxalic ions. Plutonium oxalate is converted to plutonium nitrate and oxalic acid. This latter decomposes itself into H₂O, CO₂, and NO₂:

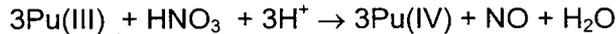


These reactions are catalyzed by Mn^{2+} ions.

Since Pu nitrate undergoes prolonged boiling and considering the high acidity of the medium, Pu(IV) nitrate is oxidized and gives Pu(VI) (as PuO_2^{2+}) nitrate as the following reaction:



The medium being highly acid, Pu(III) is itself oxidized into Pu(IV):



Therefore, at the end of the evaporator, the concentrates contain Pu at valency VI as $PuO_2(NO_3)_2$. The above severe operating conditions, (high acidity, high temperature and long residence time) necessary for the required chemical conversions are also conditions that can promote red oil formation and decomposition."

Type: Thermosiphon evaporator connected to a rectification column with bubble cap trays.

Operating temperature:	120-122°C
Operating pressure:	Near atmospheric
Type of Internals:	Multiple Bubble-cap trays
Heated by:	Pressure controlled steam
Heat removal by:	water cooled condenser

Feed:	Continuous
Distillate removal	Continuous
Bottoms removal	Continuous

Hence the Areas where conditions necessary for ROE could exist can be summarized as follows:

- Organics if present will remain in contact with acid for a relatively long time.
- High operating temperature, 122°C (251.6°F).
- High acid concentration, near azeotrope.
- High heat source temperature.
- High tube wall temperature.
- Failure of cooling in condenser CND 3200 will increase reboiler pressure, and, therefore, the temperature above its normal 122°C (251.6°F).
- Any obstruction to vapor flow in column or the vapor line will increase reboiler pressure.
- An exothermic reaction in EV 3000 will add to heat input from steam and may exceed condenser CND 3200 capacity, causing increased back-pressure.

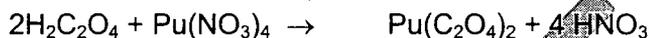
5.3.4.1 Summary of ROE Risk in the KCD Unit

The risk of ROEs in the KCD is judged to be significant conditional on organic material being present. If organic material (e.g., TBP) enters this unit, which is operating at high temperature with high nitric acid concentration coupled with long residence time increases the likelihood that the essential conditions for a ROE will be fulfilled. This is

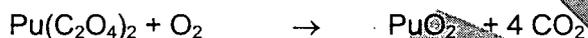
especially true if there is an equipment failure leading to loss of control of some vital parameter like temperature or adequate venting. Possible ROE scenarios that could occur in EV 3000 are analyzed further in Chapter 6.

5.3.5 Oxalic Precipitation and Oxidation Unit (KCA)

The function of the precipitation and oxidation unit is to receive purified plutonium nitrate from the purification cycle, then convert the nitrate to oxalate by reacting it with oxalic acid and precipitate out the oxalate. The operation is shown in Figure 5-6. The nitrate solution is received in batches and reacted with oxalic acid at 60°C (140°F) in the precipitators PREC 5000 and PREC 6000. The plutonium oxalate precipitate is carried by the mother liquors to the filter FLT 7000 where it is filtered, washed, and dewatered before entering the heated rotary furnace. The washing of the cake is done in-situ with a wash solution supplied by a nozzle. The flow diagrams in the LA indicate that concentrated nitric acid is used as the wash solution. The rotary furnace is used to dry and calcine the filtered cake; calcination converts the oxalate to the oxide. The LA provides the process chemistry for the nitrate to oxalate reaction as follows:



and the calcining reaction:

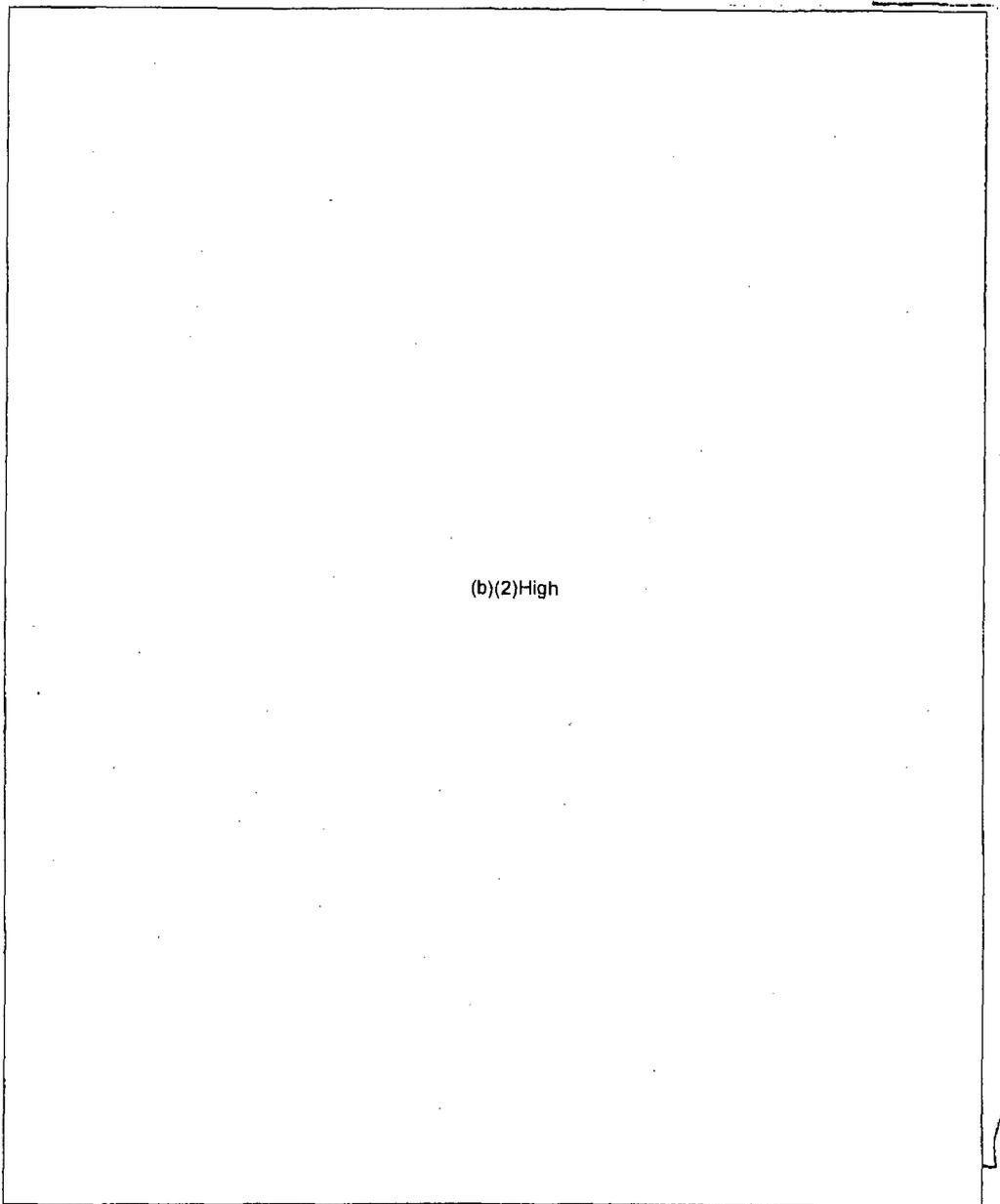


A ROE can only occur if organic material is transferred to this unit. Since the likelihood of organics reaching the KCD is judged to be low, the same also holds true for the KCA unit.

However, conditional on organic material, e.g., TBP, making its way to the KCA unit, the main areas where conditions necessary for ROE could exist in this operation are as follows:

If the solution that is fed to the precipitator contains organics, then due to the vortex created in the precipitator by the rotation of a magnetic rod driven by a static motor (as stated in the LA on page 11.2.8-4), insoluble organics will be dispersed along with the solids. Depending on the solids' surface properties, the organics may preferentially wet the solids. The aqueous wash will not adequately wash the organics from the solids and it is not unusual in such processes to discharge wet cakes containing a substantial quantity of liquid from a filter. The furnace operates at a high temperature that is substantially higher than the reference 130°C where a ROE can be initiated.

~~Official Use Only~~



(b)(2)High

EX 2
High

The two zone drying and calcination furnace is designed to provide the conditions of high temperature and long residence, especially in its calcining zone. The calciner (FUR 8000) is a multi-zone annular cylindrical electrically heated furnace. Its first zone is used as a dryer, followed by a higher temperature calcining zone. Wet plutonium oxalate from filter FLT 7000 is fed continuously to the drying zone where plutonium oxalate is dried at 250°C (482°F) for at least 10 minutes. Solids are moved into the calcining zone by an internal screw mounted axially in the cylinder. In the calcining zone, dried powder is further heated to its calcining temperature, of 450°C (842°F), and dried for at least 30 minutes.

~~Official Use Only~~

According to the LA, "the furnace consists of an annular cylindrical body, which contains an array of heating resistors and thermocouples, a screw conveyor that is driven by a motor located outside the glovebox for moving the powder, and a filtration system to filter the offgas through candle type filter. The furnace has two main sections heated by [electrical] resistors: a drying zone where the Pu oxalate is dried and a calcinations zone where the oxalate is transformed into PuO_2 . The temperatures of the drying and calcining zones are regulated independently. The effectiveness of the calcinations process is controlled by a combination of residence time and temperature. The speed of rotation of the screw is adjusted to maintain the required residence time in the drying and calcining zones based on furnace temperature. The gases produced during drying and calcinations of the Pu oxalate cake (CO_2 and steam), along with excess oxygen, scavenging nitrogen gas, and the air from upstream and downstream processes are removed by an offgas system."

The LA describes the calciner design in some detail, but does not include process and instrument diagrams for the system. However based on similar industrial equipment and the information available to BNL, we assume the following calciner design:

- The gas flow path is sized for expected generation of a large gas flow.
- Because of the difficulty of sealing such solids handling equipment, the calciner is operated under negative pressure (100% capacity exhaust fan) and most likely not designed to withstand substantial internal pressure.
- Internally mounted filters are described as non-clogging. The filter assembly consists of three stainless steel candle type filters and a second in-line filter made of sintered stainless steel; the process flow sheet shows three segments. The candle type filters are unclogged during operation by sequential air pulses with compressed, super dry air from the Instrument Air System (IAS).
- Air is added at the outlet end and flows in counter-current fashion to the solids flow.

Vent Design:

Based on the process flow sheets for the KCA unit, the vent path from the calciner body to the pair of exhauster fans is as follows:

- Gases are filtered in internal segmented filter element banks, FLT 8300.
- They are then chilled to lower the dew point below ambient, CND 8400.
- Chilled gases are de-entrained in demister vessel DMST 8500, which has provision to wash the demisting element to prevent them from clogging. (It is not clear if the wash is intermittent or continuous).
- The gases are superheated by an electric heater to avoid clogging of the downstream filter.

- They are then filtered through two HEPA filters in series, FLT 8520 and FLT 8530.
- The gases are finally exhausted by a 100% capacity exhaust fan with an installed spare that provides the driving force to induce the negative pressure on the furnace.

Areas where conditions necessary for ROE could exist

The temperature, around 450°C (842°F), in the calciner is far greater than that normally required to initiate red oil reactions. Conditional on TBP being present in the feed, and nitric acid with the feed, TBP will decompose. Thus the safety issues are principally related to the size and reliability of the vent system, specifically an accurate estimate of the amount of gas evolution and pressure drop through the system.

5.3.5.1 Summary of ROE Risk in the KCA Unit

The possibility of a ROE in the KCA exists if organic material manages to reach this unit. However, by design, this unit is designed to handle large volumes of gas flow so even if some red oil is formed the chances of a high-pressure event are low. Therefore, further quantitative analysis was not performed for this unit. Instead, the resources at BNL were focused on the KPC and KCD units.

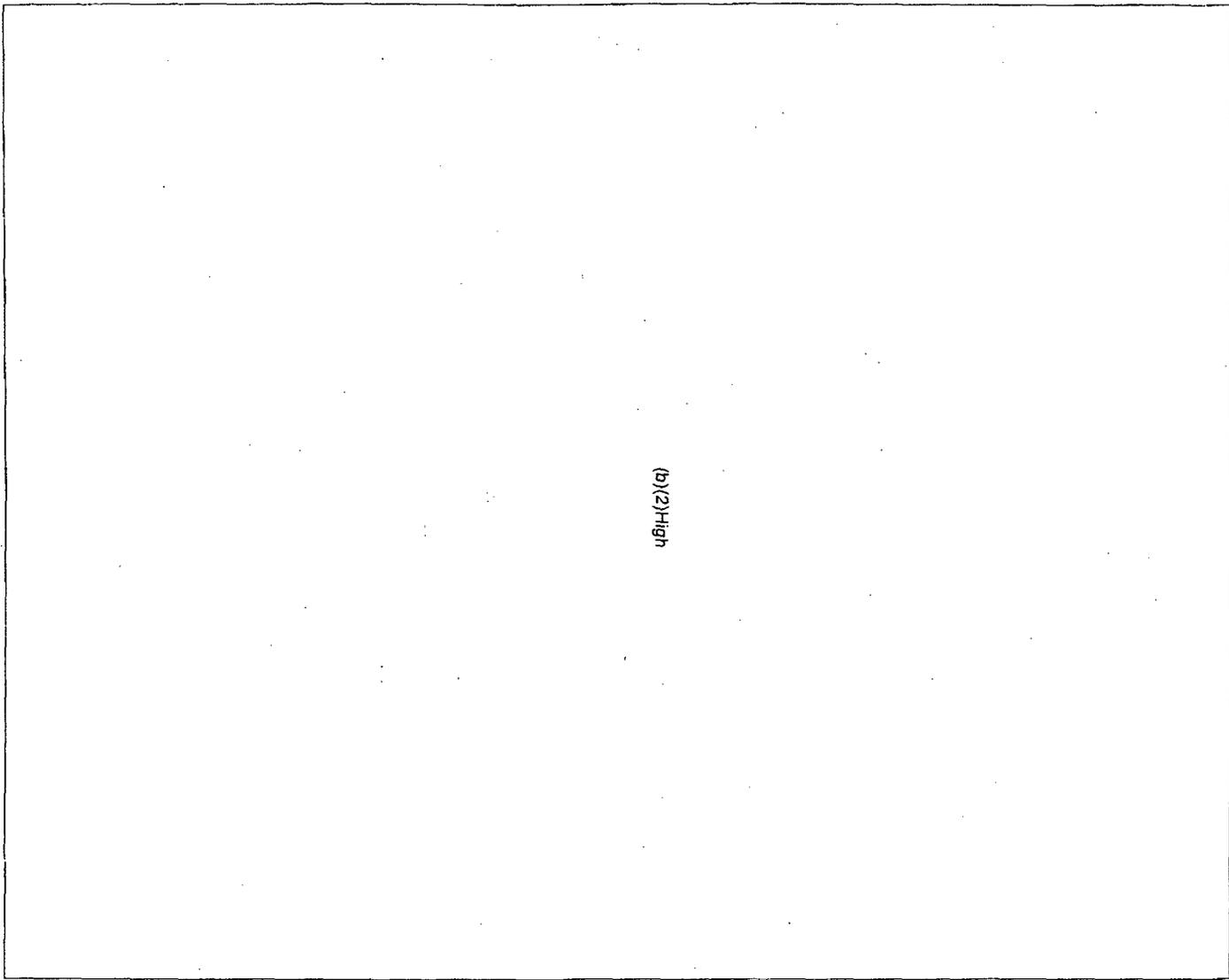
5.3.6 Slab Settler

The Slab Settler KPA SET 3300 that is provided at the back end of the KPA is a key piece of safety equipment. Its function is to prevent any organic material that is entrained with the aqueous phase as it leaves the plutonium diluent pulse washing column from entering the KCD unit evaporator. The conditions in the KCD unit's evaporator under its normal operating condition are such that ROE is inevitable if sufficient organic material is present. It is operated at high temperature, high nitric acid concentration and long residence time, conditions that promote organic/nitric acid reactions. The LA and the ISA documentation take credit for the slab settler barrier as an IROFS.

The slab settler is a passive device that separates the lighter organic phase from the heavier aqueous phase based on density difference alone. When operated properly it is an effective barrier against flow of organic phase to the oxalic acid treatment area. The ISA Summary indicates (page 4.2.6-15): "In the settler, any organic phase will separate since the organic and aqueous phases are non-miscible. The lighter organic phase will rise to the top of the liquid while the aqueous solution remains on the bottom. The solution remains in the slab settler long enough to ensure separation of any organic solvent from the solution."

A schematic drawing of the slab settler, obtained from the licensee, showing the layout of the design is shown in Figure 5-7. A brief description of the slab settler is provided in the ISA Summary and in the LA (page 11.2.6-15).

~~Official Use Only~~



(b)(2) High

EX 2
High

~~Official Use Only~~

Interface location:

The interface location on such designs is only a function of relative densities. The design principles, which the designers have followed, are:

1. Heavy (Aqueous) phase is removed from a low point in the settler.
2. Aqueous phase is looped with a vent at the highest point
3. Light (Organic) phase is an overflow
4. Organic phase overflow and the top of the aqueous phase loop heights are such that under all conceivable density ratios the interface height is well above the aqueous phase removal level.
5. All flows have equal, usually very low, frictional pressure drop. In other words, pressure balance (defined below) is a function of densities only and not the flow rates.

If the above principles are followed the interface location does not vary with individual phases or the total flow rate. In cases where the light phase content of the feed is zero, the light phase outflow is consequently zero. No instrumentation is required to operate this equipment due to its inherent passive design features.

Pressure balance:

With equal pressure above the light phase and the top of the heavy phase loop, the pressure balance has the following equality.

$$(X_1 - X_4) \rho_1 = (X_3 - X_4) \rho_1 + (X_2 - X_3) \rho_2$$

where

- X₁ = Heavy phase loop height
- X₂ = Light phase overflow height
- X₃ = Interface height
- X₄ = Clearance of heavy phase outlet (Or Datum level)
- ρ₁ = Heavy phase density
- ρ₂ = Light phase density

It should be noted that the equation above does not contain flow rates; only construction dimensions and densities. This is illustrated in Figure 5-8 below where the relative dimensions and locations of the different levels of the heavy and light phases are shown.

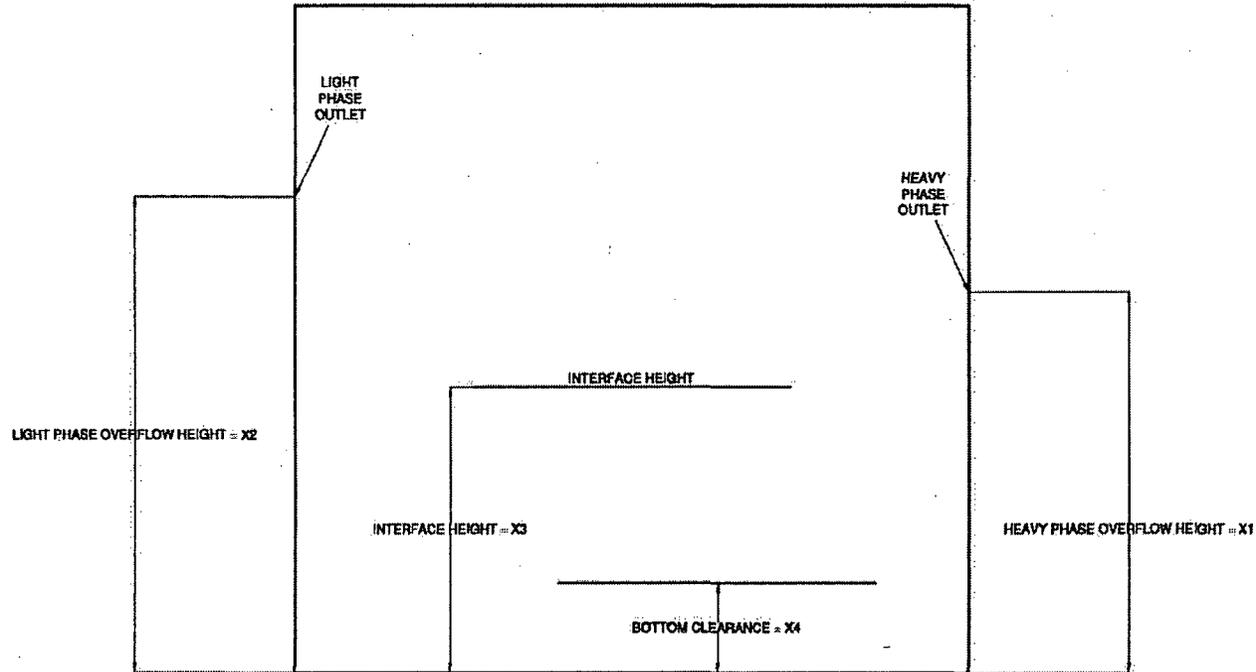


Figure 5-8. Slab settler dimensions and locations of the levels of the light and heavy phases.

Given the current slab settler design, the respective locations of the baffle and the outlets of the organic and aqueous phases are shown below:

- separation baffle 80 mm from the bottom (X_4),
- aqueous outlet 435 mm from the bottom (X_1),
- organic overflow 450 mm from the bottom (X_2).

These values are input into the equation above along with various values of the aqueous and organic phase densities to evaluate the interface height X_3 .

The results are shown in Table 5-2 below, which shows the interface location for various organic and aqueous densities. The organic phase seal remains intact as long as the interface location is above the bottom of the partition plate, 80 mm.

Table 5-2. Calculation of Interface heights as function of phase density.

Case	Aqueous Phase Density (kg/m ³)	Organic Phase Density (kg/m ³)	Interface Height (mm)	Seal Broken
1	1012.2 (0.5M HNO ₃)	860.0	350.2	No
2	1012.2	855.6	353	No
3	1012.2	825.0	368.9	No
4	1012.2	800.0	378.4	No
5	1026.9 (1M HNO ₃)	875.0	348.6	No
6	1026.9	868.0	353	No
7	1026.9	825.0	373.7	No
8	1026.9	800.0	382.1	No
9	1086.1 (3M HNO ₃)	925.0	348.9	No
10	1086.1	918.0	353.1	No
11	1086.1	825.0	387.6	No
12	1086.1	800.0	393.1	No

If the ratio of organic phase density to aqueous phase density is greater than 0.9595, the seal is broken. If the ratio of these densities is less than 0.9595, then the seal remains intact. Since the ratio of pure TBP density to pure water density at 25°C (77°F) is 0.97 and there is going to be some admixture of the (lower density) diluent HPT in the organic phase with TBP (which will lower the organic phase density) and of nitric acid with water in the aqueous phase (which will increase the aqueous phase density) it is clear that the slab settler will continue to work, i.e., the seal will remain intact as long as the densities remain in the range considered. This analysis is limited as it is a static head analysis, which assumes that equilibrium is reached to allow the phases to separate. However, the formation of emulsions or of a rag layer, etc. may defeat the normal operation of the settler. These possibilities are examined further in Chapter 6.

The ISA Summary indicates (page 5.3.6-63) "To ensure the slab settler operates as intended, operators ensure, via an IROFS administrative control, that the slab settler is loaded with aqueous solution prior to start-up and redundant IROFS density instrumentation is provided to ensure (1) the density interface on the settling side of the

slab settler does not drop below the weir height, (2) the settler is not initially filled with the lighter density material, and (3) the lighter material is not sent to the KPA oxidation column." Although the slab settler is based on intrinsically safe design principles (dependence on gravity and density difference alone), its proper operation depends on operational procedures being correctly followed by the operators, hence it is difficult to classify it as a purely passive safety device.

The impacts of possible failures of the slab settler, due to operational errors or due to holes and leaks in the baffle plate that may be caused by corrosion or other causes, are analyzed in Chapter 6.

5.4 Overall Design Strengths and Considerations

The discussion below offers some considerations related to the strengths of the design, possible concerns and deficiencies, and data that is needed to do a more detailed assessment.

5.4.1 Design Strengths

The process design has substantially reduced the risk of uncontrolled decomposition during normal operation by:

- Use of stable pure HPT as a diluent versus kerosene, which had been used before in other similar extraction applications.
- Use of "wash columns" to wash the aqueous nitric acid phase with the diluent and similarly the use of columns with water or dilute acid to wash the organic phase.
- Operation of first stage evaporation under vacuum, at a temperature substantially below 130°C (266°F) (the temperature suspected by many investigators as a critical temperature, above which uncontrolled runaway reactions can start).
- Continuous removal of TBP decomposition products by alkali treatment of the entire solvent phase.
- The entire set of IROFS controls that implement the red oil prevention strategies previously discussed in Chapter 4, i.e., prevention of TBP migration to undesired process vessels, heat transfer, and evaporative cooling.

As is well known, the frequency of events that can impact safety during normal continuous operation of a well designed and operated plant is low. Experience indicates that most safety-related events take place due to or during intermittent operations, for example, start-up or shutdown operation. This effort of analyzing the risks associated with the design of the MFFF provides insights into whether the above-mentioned basic design elements reduce the event frequency, including expected upsets, the deterioration of equipment such as fouling of heat exchange surfaces, instrument and other equipment failures, and startup and shutdown.

5.4.2 Overall Design Considerations

We are principally concerned with two types of events:

- Formation of red oil in the equipment or process under consideration
- Contribution to a condition that may lead to red oil formation in downstream equipment such as allowing passage of organics in the aqueous phase or acid in the organic phase as examples.

Conditions that can potentially lead to the above events are as follows:

1. **Incomplete Phase Separation.** This is characterized as intermittent contamination of phases, where the outlet concentration of a phase may exceed the solubility limits by several times. Trace amounts of impurities, in particular, have a profound impact on interfacial tension and thus separation ability. Anecdotal information from the industry based on an informal telephone survey indicates that this event may have a frequency ranging from around 0.5 to 3 events per year. This phenomenon includes emulsion formation which differs from simple inadequate separation. Inadequate separation can be usually corrected by providing adequate settling time and/or lowering interface velocities. Emulsions on the other hand are difficult to break and sometimes require additional corrective measures such as heating, pH adjustment, addition of anti-emulsion additives, etc. Emulsions are formed by a combination of excess mixing energy per mass and presence of surface-active ionic compounds.
2. **Flooding:** under normal condition in an extraction column the two phases flow in opposite directions; that is, the droplets of the phase to be dispersed flow in the opposite direction to the bulk phase flow. This works as long as the buoyancy due to the density difference can overcome the drag forces caused by linear velocity, viscosity and other fluid mechanics parameters. Flooding in an extraction column is defined as a condition under which one phase is prevented from flowing in the opposite direction to the other phase. In other words, it drags the other phase with it. This may occur when there is an increase in velocity due to higher flow or restricted flow path (plugging), or increased viscosity due to lower temperature, higher salt concentration or lower diluent concentration. Air-lift failure, interface control failure or lower density difference can lead to this condition.
3. **Rag layer formation:** In most liquid-liquid operations, ionic and surface active impurities tend to collect at the interface. Because the light liquid is removed from near the top of its layer and similarly the heavy liquid is removed from the near the bottom of its layer, the rag layer continues to build up, eventually preventing clean separation of the two phases.
4. **Incomplete Draining:** Incomplete draining of equipment such as evaporators, other process or storage vessels could lead to accumulation of the lighter organic phase.
5. **Tube wall temperature in steam heated exchangers:** Tube wall temperature is dependent on the bulk temperature of fluids of the tube and relative heat transfer coefficients on either side of the tube. If heat transfer coefficients on both sides are equal, then the tube wall temperature is close to the average of the two bulk

temperatures. In steam-heated heaters, because of relatively high steam-side heat transfer coefficients compared to the process side, the tube wall temperatures are closer to the steam temperature than the process side bulk temperature. For safety studies, the higher tube wall temperature, rather than the average bulk temperature, should be considered for the reaction initiation temperature. Fouling of heat exchanger surfaces, usually on the process side, further exacerbates the difference between the tube wall and the bulk temperature. Another concern regarding heat transfer is the relatively poor heat transfer properties of organics/solvent phases as compared with aqueous or steam phases. This issue has been discussed in NRC's SER on the CAR design [5-11] as a contributor to red oil formation in event that a phase inversion occurs due to salts getting trapped in the organic/solvent layer.

5. A critical part of the MFFF IROFS is that all vessels where a red oil event could occur are deemed to be sufficiently vented or "open." Based on the information that was available at the time this report was prepared, it seems that the ventilation system for each piece of equipment requiring venting was evaluated as being a fixed length with a fixed number of elbows, turns, valves, etc. To support the applicant's evaporative cooling strategy, a supporting document [5-12] provides the vent sizing guidelines and bases for vessel in which a ROE may conceivably occur.

5.5 References

- 5-1. Shaw Areva MOX Services, "MFFF License Application," December 17, 2007.
- 5-2. Shaw Areva MOX Services, "ISA Summary," December 17, 2007.
- 5-3. Shaw Areva MOX Services, "Fire Hazard Analysis for the MFFF," Report No. DCS01 ASI DS ANS R 10480 0.
- 5-4. Shaw Areva MOX Services, "Preliminary Accident Analysis," Report No. DCS01 ZJJ CG ANS 38317 C.
- 5-5. Shaw Areva MOX Services, "Preliminary Hazards External Man-Made Event Screening," Report No. DCS01 RRJ DS ANS H 38307 C.
- 5-6. Shaw Areva MOX Services, "HAZOP Analysis for KPC Acid Recovery Unit," Report No. DCS01 KPC DS ANS H 38347-1.
- 5-7. Shaw Areva MOX Services, "Basis of Design for Electric Systems," Report No. DCS01 AAJ DS E 40111-2.
- 5-8. W. W. Schulz, J. D. Navratil, and A. E. Talbot, eds. *Science and Technology of Tributyl Phosphate: Volume I, Synthesis, Properties, Reactions, and Analysis*. Boca, Raton: CRC Press, Inc., 1984.
- 5-9. T. Boublik and K. Kuchunka, Collection Czechoslov Chem. Commun., Vol. 25, pp. 579-582, 1960.

- 5-10. E. E. Ludwig, Applied Process Design For Chemical and Petrochemical Plants, Vol. 2, 3rd Edition, page 220, Gulf Publishing Company, Houston, TX, 2002.
- 5-11. U.S. Nuclear Regulatory Commission, "Final Safety Evaluation Report on the Construction Authorization Request for the Mixed Oxide Fuel Fabrication Facility," NUREG-1821, March 2005.
- 5-12. Shaw Areva MOX Services, "Vent Sizing Guidelines for Vessels Subject to Nitrated TBP Degradation," Report No. DCS01-KKJ-DS-CAL-F-10803-A.

DRAFT

6. RED OIL SAFETY STRATEGY – AN OVERVIEW

As detailed in Chapter 4, the safety strategy adopted by the MOX facility is mainly preventive, i.e., it reduces the likelihood of a ROE rather than simply trying to mitigate its consequences should it occur. It relies on three different strategies. The implementation of the appropriate strategy depends on the operational constraints associated with each process vessel. These strategies are recapitulated below:

1. **TBP Prevention** – This strategy involves segregation of TBP (in a separate phase) from acid-bearing process equipment and limiting the amount of TBP in soluble phase to prevent runaway TBP-nitric acid reactions. For those process vessels not normally containing TBP, and where separate phase TBP can be effectively segregated considering credible process upsets, a safety strategy that prevents TBP migration (separate phase) into the vessel is employed (e.g., process vessels in the KCA, KCD, KPA, KPC, KWD, and LGF units). This is accomplished by design (no credible pathways to receive TBP) or through the implementation of IROFS controls. These controls consist of process and drip tray sampling controls and associated IROFS to maintain sampling integrity, organic phase detection controls including density monitors, and the slab-settler. The objectives of these controls are to prevent the propagation of separate phase TBP to downstream vessels and limit the soluble amount of TBP transferred by aqueous phase.
2. **Heat Transfer** – This strategy relies on adequate heat transfer from TBP-bearing vessels to the surroundings to prevent runaway TBP-nitric acid reactions. Simply stated, the heat transfer must exceed the energy generation of the system to ensure that a thermal runaway does not occur. Experiments have shown that the heat of reaction, even if small at low temperatures, will eventually lead to a runaway reaction if the vessel is adiabatic and no means for cooling is provided. A thermal runaway reaction will not occur when the heat removal rate exceeds the heat production rate. This is the basis of the heat transfer strategy applied to various process vessels in the KPA, KPB, KWD, KWS, and LGF units. For those vessels where the heat transfer strategy is employed to prevent red oil explosions, the following IROFS controls are used: vessel geometry, process temperature controls, process vessel off-gas venting, and reagent (diluent) sampling controls. In addition, to ensure the effectiveness of the heat transfer strategy, the HVAC system is designed and controlled in a manner to limit the temperature in the associated rooms/cells.
3. **Evaporative Cooling** – This strategy ensures that the heat input from chemical reactions and other sources is limited to that which can escape the vessel via evaporation. This requires maintenance of an aqueous phase in TBP-bearing vessels to ensure evaporative cooling to prevent runaway TBP-nitric acid reactions. For evaporative cooling to be effective, an aqueous phase should be constantly present and adequate venting be available. Furthermore, the depth of the organic layer must be limited so as to not impede the heat transfer due to aqueous phase boiling. It should be noted that the solution boiling temperature can increase as water is boiled off and the remaining nitric acid becomes more concentrated, up to the point where the azeotropic limit of nitric acid is reached (68.4% nitric acid, boiling point = 122°C [251.6°F]). Therefore, the presence of an

aqueous phase below a limited depth TBP-bearing organic phase, or in the well-mixed confines of the vessels, combined with adequate venting capability, provides assurance that TBP-nitric acid reactions will not result in red oil explosions. For the vessels in which the evaporative cooling strategy applies (i.e., process vessels in the KPC and KWD units), it is important to understand the source of separate phase TBP. The following controls are used to ensure effective evaporative cooling strategies: administrative flushing controls to ensure the maximum TBP layer depth will not be exceeded; process level controls (both active engineered and administrative) to maintain the minimum water-to-TBP mass ratio; process temperature controls (both active engineered and administrative) to maintain process solution temperatures within permissible limits; process vessel off-gas venting to ensure adequate venting; and reagent sampling controls to maintain the veracity of assumptions made in the evaporative cooling analysis regarding the less reactive nature of the diluent. Selection of HPT diluent is an important factor in maintaining the evaporative cooling strategy.

As indicated in Chapter 3, to ensure the effectiveness of these preventive strategies, a semi-empirical model describing the heat generation for TBP/nitric acid reactions was developed by the applicant to specifically account for conditions present in the AP process [6-1]. This model was developed to address the catalytic effects of plutonium, uranium, and zirconium in the low temperature region and is based on data resulting from over 80 individual experiments that examined the effects of temperature, nitric acid concentration, uranium concentration, plutonium concentration, and zirconium concentration on the rate constants. The catalytic effect of other elements was not considered since their mass fractions were judged to be insignificant. Using empirical correlations obtained from the experimental results, the corresponding heats of reaction were established at various solution temperatures. The heat associated with plutonium and americium decay was also accounted for in the development of the TBP/nitric acid reaction heat generation model. This model was then used as a basis for development of safe operating regimes for both the heat transfer and evaporative cooling strategies.

6.1 TBP Prevention Strategy – Component Specific Application

Prevention controls consist of process and drip tray sampling controls and associated IROFS controls to maintain sampling integrity, organic phase detection controls, and the slab-settler, which prevents the propagation of separate phase TBP to downstream vessels. Process sampling controls ensure that the maximum concentration of TBP in solution is satisfied below some limits prior to transferring solutions to vessels where TBP in large quantities should be prevented. This also applies to drip trays where TBP may be leaked and subsequently transferred to a vessel where TBP has to be prevented. IROFS process sampling controls are taken from the following vessels to protect downstream units vulnerable to a red oil event: both KCA batch constitution tanks (TK-1000 and TK-2000) to protect the KCD unit and KPA control tank (TK-9100) to protect the KPC unit. IROFS drip tray samples are taken from drip trays in the KCD and KWG unit to protect the KCD unit which is vulnerable to a red oil event. Additionally, IROFS drip tray samples are taken at KPA drip trays which may contain TBP to protect against a steam jet draining these trays. Thus, these sample points and the associated administrative IROFS required to ensure the sample is representative of the contents of the tank (i.e., vessel isolation, vessel homogenization, sample line purging, sample vial

traceability, laboratory sampling process, and communication of results from laboratory to the control room) ensure red oil explosions are highly unlikely.

At the KPB alkaline waste tank, organic phase detection controls detect any separate phase TBP that accumulates in the vessel via redundant IROFS density transmitters and controllers, along with automatic action to shut off the transfer pump to the KWD alkaline waste tank. This prevents the transfer of separate phase TBP to the front-end of the KWD high alpha azide destruction vessels. Administrative procedures provide guidance to the operator regarding appropriate actions when low density solution is detected (i.e., commence flushing operations).

To ensure the IROFS are not challenged, operators periodically purge organics from this process vessel, via an administrative control, to prevent TBP accumulation that triggers the density IROFS.

The passive design features of the slab settler tank in the purification cycle is credited as an IROFS to prevent the propagation of separate phase TBP downstream to the back-end of the purification cycle and on to the KCA unit. To ensure that the slab settler operates as intended, operators ensure, via an IROFS administrative control, that the slab settler tank is loaded with aqueous solution prior to start-up and redundant IROFS density instrumentation is provided to ensure (1) the density interface on the settling side of the settler does not drop below the weir height, (2) the settler is not initially filled with the lighter density material, and (3) the lighter material is not sent to the KPA oxidation column. Thus, the combination of the passive design of the KPA slab settler and the active engineered redundant density instrumentation ensure red oil explosions are highly unlikely to occur in downstream units due to separate phase TBP.

To ensure that the soluble TBP passing through the KPA slab settler does not accumulate to the degree of becoming a separate phase in the KCD evaporator, process sampling is performed upstream in the KCA batch constitution tanks to confirm the amount of soluble TBP is sufficiently low. Thus, these sample points and the associated administrative IROFS required to ensure the sample is representative of the contents of the tank (i.e., vessel isolation, vessel homogenization, sample line purging, sample vial traceability, laboratory sampling process, and communication of results from laboratory to the control room) ensure red oil explosions are highly unlikely in the KCD unit.

Table 6-1 provides an example list of the major components and the associated IROFS that act as barriers for prevention strategies. A complete listing of all vessels/equipment protected by the TBP prevention strategy is provided in Appendix B.

Table 6-1. Prevention strategy IROFS, Example of Major Prevention Strategy Barriers.

Component	IROFS	Protected Components	Comment
KPA-TK-9100 [protected by the heat transfer strategy and it provides TBP prevention strategy]	Redundant KPA*SMPT9100	KPC-TK-1000	Organic layers and soluble organics
Slab Settler 3300 [protected by heat transfer strategy and it provides prevention strategy] Redundant Density transmitters (need ID number) Administrator control to preload Settler and some drip trays	Passive Slab Settler KPA-DT3300A/B (see note 1) Admin control	KPA-CLMN-6000 KPA-CLMN-6500 & KPA-TK-7000	Organic layer
KCA-TK-1000 & KCA-TK-2000			Soluble organics
KCA-TK-1000 & KCA-TK-2000 [protected by prevention due to slab settler and provides prevention for KPA columns 6000 and 6500]	Redundant KCA*SMPT1000 and Redundant KCA*SMPT2000	Whole process KCA and Whole process KCD	Soluble organics
KPB-TK-3000 [protected by heat transfer strategy and it provides prevention strategy] Density transmitters	Redundant KPB*DT3001 A&B	KWD-TK-4010	Organic layer

1. (ISA Summary page 5.3.6-63, pp 2452) states: "...redundant IROFS density instrumentation is provided to ensure (1) the density interface on the settling side of the settler does not drop below the weir height, (2) the settler is not initially filled with the lighter density material, and (3) the lighter material is not sent to the KPA oxidation column."

6.2 Heat Transfer Strategy – Component Specific Application

Heat balance calculations performed for several process vessels confirmed that during conservative upset conditions the maximum temperature rise would not be sufficient to cause the solvent temperatures to exceed their safety limit. However, for those vessels and conditions in which the temperature rise would potentially exceed the safety limit, a preventative safety strategy is utilized. The safety limit here depends on the hazard being protected against. A temperature limit of 50.6°C to 55°C (123.1°F to 131°F) is considered for vessels when both TBP and HAN are present [depending on the amount of diluent present in the vessel], and a temperature limit of 125°C (257°F) is considered for the ROE. When a component could be exposed to both hazards the lowest temperature limit is applied which provides a large safety margins for the other hazard.

To prevent the creation of flammable or explosive vapors within vessel head spaces and in venting ducts due to process temperature deviations, IROFS process temperature controls provide an element of redundancy to shutdown the process heaters and/or heating loop flow sources when a high temperature is detected. Residual heat will be dissipated primarily to the surrounding environment, thereby preventing the solution temperature from reaching its safety limit. The IROFS temperature control group consists of redundant temperature elements, temperature transmitters, temperature control valves, and automatic operated valves.

For the KPA Pu stripping pulsed column, in a condition where the temperature monitors would not be effective (i.e., prior to exceeding 60% of the LFL), two independent sets of neutron sensors, consisting of redundant radiation elements and transmitters, are used to detect an aqueous flow condition leading to this undesirable condition. At a given neutron flux ratio, these neutron detection IROFS stop the transfer of solvent and heating of aqueous and organic feeds to this pulsed column by actuating the shutdown of respective air lifts and closure of corresponding isolation valves.

The risk of exceeding the temperature safety limit as a result of heat from a transfer pump is prevented by an administrative control credited with limiting the operation of some pumps used to mix process vessels containing solvent, in turn limiting the amount of heat input from the pump work into the process fluid. These administrative controls are enhanced with process fluid temperature monitors and warnings providing operators with early detection of process fluid temperature deviations. The major components for which heat transfer strategy are applied with the associated IROFS are shown in Table 6-2. A complete listing of all vessels/equipment protected by the heat transfer strategy is provided in Appendix B.

Table 6-2. Heat Transfer strategy IROFS, Example of Major Components.

Components	IROFS	Protected Components	Comment
KPA unit Whole process to CLMN6000	Geometry of Process Vessel and pipes Process Temperature Controls Process vessel Off-Gas Venting Reagent Sampling	KPA unit: Whole process to CLMN6000	Note that as discussed in the text, use of a neutron monitor instead of the temperature monitor should be considered for KPA pulse 2000. Note that the most restrictive temperature criteria are for Pulse 3000 and 3200 due to exothermic reactions for Pu stripping by HAN, and the potential for oxidation of Pu from valence III to IV. Therefore, the red oil issue is not as much concern for heat transfer methodology [temperature limit of 48°C for Pulse 3000 and 53°C (127.4°F) for Pulse 3200].
KPB whole process	SAME AS ABOVE	KPB whole process	KPB-TANK-3000 is 200 liters and it contains some amount of Pu and U. This is a consideration for Heat transfer strategy.
KWD-TK-3010 KWD-TK-3020 KWD-TK-3030 KWD-TK-3040	SAME AS ABOVE	KWD whole process	High Alpha Waste (HAW) tanks, Pu, U, and Americium.
KWS-TK-4000 KWS-TK-5010	SAME AS ABOVE	KWS whole process	
LGF-TK-3000	SAME AS ABOVE	LGF-TK-3000	HAW

6.3 Evaporative Cooling – Component Specific Application

The concept of evaporative cooling is to ensure that the temperature in a vessel containing a TBP and nitric acid is maintained below the azeotropic limit of nitric acid (122°C). For a mixture of nitric acid and TBP within a vessel where a limited depth of separate phase TBP is floating on top of an aqueous phase, or in a well-mixed environment of a thermo-siphon evaporator, the maximum solution temperature of a TBP-nitric acid mixture for successful evaporative cooling is limited essentially to the boiling point of the aqueous phase, since any organic present consisting of TBP or TBP/HPT mixtures has a higher boiling point.

As stated above, a semi-empirical model describing the heat generation for TBP/nitric acid reactions was developed by the applicant to specifically account for conditions present in the AP process [6-1], which was then used as a basis for development of a safe operating regime for the evaporative cooling strategy.

Success of the evaporative cooling strategy requires that an aqueous phase be constantly present, as well as that adequate venting be available, and that the heat input from chemical reactions and external sources be limited to that which can escape the vessel via evaporation. Furthermore, the depth of the organic layer must be limited so as to not impede the heat transfer due to aqueous phase boiling. In addition, a limited heat input is required such that aqueous phase evaporation does not exceed the capability of the vessel vents or the ability to maintain adequate aqueous mass. Based on the calculation shown in Chapter 3, the parameters to be controlled and their associated limits, in the absence of HPT, for the success of the evaporative cooling strategy are as follows:

- Minimum water-to-TBP mass ratio of 1:1
- Maximum TBP layer depth of 34 centimeters (cm)
- Maximum process solution temperature of 122°C (251.6°F)
- Open (adequately vented) system

In the presence of 5% HPT, the maximum TBP layer depth is reduced to 26 cm. It should also be noted that, in the absence of a separate aqueous phase, if the initial solution temperature is limited to a maximum of 80°C (176°F), over 600 minutes (10 hours) is required before the solution temperature resulting from TBP/nitric acid reactions ramps up exponentially. Injection of an aqueous phase (at ambient temperatures) to fulfill the 1:1 minimum water-to-TBP mass ratio at any time during this interval will quench the reaction and maintain the system within a safe operating regime.

IROFS for the Evaporative Cooling Strategy have been described in Chapter 4. An example of IROFS density controls for the detection of HPT is in the KPC buffer tank. IROFS sampling in the purification cycle control tank ensures that no separate phase TBP will enter the KPC. IROFS density controls in the KPC buffer tank therefore would detect HPT and prevent HPT from passing downstream, so that the maximum permissible TBP layer depth for applicable downstream vessels is 34 cm.

The major components that are protected by the evaporative cooling strategy are shown in Table 6-3. A complete listing of all vessels/equipment protected by the evaporative cooling strategy is provided in Appendix B.

6.4 Red Oil Scenario for KPC- EV 2000

KPC-EV2000 is a natural recirculation thermo-siphon type boiler, which utilizes pressurized super heated water from the Hot Water System (HWS) as a heating fluid. Nitric acid vapor distillates from this evaporator are condensed and routed to a feed buffer pot that decouples operation of the first evaporator from the second evaporator.

The KPC EV2000 operates under vacuum. The normal process temperature is below 66°C and the normal super heated hot water temperature is 105°C (221°F). The hot water system temperature is equipped with controls to ensure a maximum temperature of 122°C (251.6°F) is not violated. The red oil prevention strategy applied to EV 2000 is evaporative cooling.

6.4.1 Conditions Necessary for Red oil Explosion

The following two conditions are necessary for a viable ROE scenario to occur:

1. A rising process temperature above 80°C (176°F); this can be due to (1) inability to maintain the hot water system temperature below 122°C (251.6°F), (2) the occurrence of a heat exchanger tube rupture, or (3) exposure to external heat sources, including global initiators such as fire.
2. Failure of evaporative cooling to successfully mitigate the event and prevent the occurrence of ROE.

The necessary conditions for successful evaporative cooling as noted in the ISA Summary and discussed in Section 6.3 above are provided below. Failure of evaporative cooling is assumed if one or more of the following conditions are not met:

- Minimum aqueous-to-TBP mass ratio of 1:1
- Maximum TBP layer depth of 34 centimeters (cm)
- Maximum process solution temperature of 122°C (251.6°F)
- Open (adequately vented) system

Based on the process flow rates, failure to flush the system every 6 months can lead to an accumulation of TBP that will violate the condition of maintaining a minimum aqueous-to-TBP mass ratio of 1:1. Hence, failure to flush every 6 months is also a condition for a ROE to occur.

The following sections provide an evaluation of how each of the conditions for evaporative cooling could be violated. Due to dependency among these conditions they are categorized into two groups. The criteria for the aqueous-to-TBP mass ratio and the depth of the TBP layer are in one group and the venting and process temperature criteria are in the other group. The following sections discuss possible ways in which the minimum aqueous-to-TBP mass ratio and maximum TBP layer depth criteria as well as the maximum process solution temperature of 122°C (251.6°F) or adequate venting criteria could be violated.

Table 6-3. Evaporative Cooling Strategy IROFS, Components Applied, and Components Protected.

Components	IROFS	Protected Components	Comment
KPC-TK-1000	Density Measurements	KPC-TK1500	
KPC-TK-1500	1. Administrative control for flushing every 6 months 2. Redundant temperature transmitters with alarm and operator action		
KPC-TK-3000	1. Administrative control for flushing every 6 months 2. Redundant temperature transmitters with alarm and operator action	KPC-TK-3000	KPC-TK-3000 is fed from EV-2000 and KPC-TK-1500
KPC-EV-2000	1. Administrative control for flushing every 6 months 2. Redundant process level and temperature controls with controllers and air operated valves (AOVs) 3. Redundant process temperature controls with controllers and AOVs in case of tube rupture	KPC-EV-2000	KPC-EV-2000 is fed from KPC-TK-1500
KWD-TK4020	1. Administrative control for flushing every 12 months 2. Redundant process level controls with controllers and AOVs 3. Redundant process temperature controls with controllers and AOVs	KWD-TK4020	
KWD-TK4030		KWD-TK4030	
KWD-TK4040		KWD-TK4040	
KWD-TK4050		KWD-TK4050	

6.4.2 Minimum Water-to-TBP Mass Ratio and Maximum TBP Layer Depth

To assist the discussion relating to TBP accumulation, the following definitions are helpful:

Normal TBP accumulation: accumulation of a small amount of TBP which was dissolved in the aqueous phase and the accumulation by droplets of solvent that are mechanically entrained with the aqueous phase.

TBP accumulation due to an upset condition: severe process malfunction resulting in the transfer of a large volume of solvent. The malfunctions could include failure to maintain the interface level between aqueous and organics phases as well as such phenomena as the formation of an emulsion, a third phase formation, and phase inversion in pulse columns. Such rapid accumulation of TBP is referred to as upset TBP accumulation in contrast to normal TBP accumulation.

The potential for ROE is, therefore, discussed separately for normal accumulation and accumulation under upset condition. ROE during normal accumulation is discussed in Section 6.4.2.1 and ROE under upset condition is discussed in Section 6.4.2.2.

6.4.2.1 ROE in EV 2000 under Normal TBP Accumulation

High solution temperature and failure of the evaporative cooling strategy is required for ROE to occur under the normal TBP accumulation condition in EV 2000.

High temperature could occur due to loss of temperature control in the HWS or heat exchanger tube rupture. High temperature could also occur as a result of an exothermic chemical reaction and radioactive heating especially if the amount of TBP is not controlled through regular flushing of the vessels. This latter mechanism is considered less likely than other mechanisms since a slow increase in solution temperature could be measured by KPC-THC-2000A/B, which would allow the operator to take corrective actions.

The first condition (Section 6.4.1) in evaporative cooling, i.e., ensuring the minimum aqueous to TBP ratio of 1:1, is maintained by flushing out the vessels every six months. The second condition in evaporative cooling, i.e., maximum TBP layer height of 34 cm, during normal TBP accumulation is maintained both by flushing out the vessels every six months and by ensuring that the level in the evaporator EV 2000 never falls below the low level limit which ensures that the evaporator contains at least 42 liters of solution. This strategy is based on the maximum calculated accumulation rate of separate phase TBP, which indicates that at most 21 liters of TBP would be accumulated in the evaporator before the semi-annual flush out of the system. In this manner, the total amount of TBP transferred from the first evaporator in the KPC unit to the KPC concentrates tank would be about 42 liters/year. Semi-annual flush-out of the first KPC evaporator, the KPC concentrates tank, and the KPC feeding tank, collectively, will then ensure that no more than 21 liters of TBP is ever present in any of these vessels. By ensuring that the total volume of the solution in EV 2000 does not exceed 42 liters, one could ensure that the aqueous-TBP ratio is maintained. Similarly, the maximum TBP layer depth of 34 centimeters is also ensured by the accumulation rate of TBP and the evaporator design dimensions as well as by the flushing-out procedures.

The probability that the vessels are not flushed out in six months is conservatively assumed to cause an unavailability of evaporative cooling for six months when the next flushing out is scheduled. The failure probability/unavailability for level controls is estimated through standard fault tree methodology. The level transmitters KPC-LT-2000A/B and low level controllers KPC-LLC-2000A/B will close KPC-AOV-2003A/B to terminate the HWS. Standard fault tree modeling is used to also evaluate the possibility of operating at low level when the vessel is heated.

The potential of ROE in EV2000 under normal TBP accumulation is pictorially presented in the event tree of Figure 6-1. The initiating event for this scenario represents the different ways in which the solution temperature can increase such that it can initiate a ROE if the evaporative cooling strategy fails. This can occur either due to a loss of temperature control in the HWS or a heat exchanger tube rupture. The loss of temperature control is modeled via a standard fault tree model, shown in Figure A-2, of a two train temperature control system. This system consists of the temperature elements KPC TE 2003 A/B, temperature transmitters KPC TT 2203 A/B, and temperature controllers KPC THC 2003 A/B, which signal the closure of the hot water shutoff valve KPC AOV 2003A/B. The failure of these components, based on the failure rate data shown in Table A-1 in Appendix A, is used to estimate the frequency of the loss of temperature control. The frequency of the heat exchanger tube rupture and its associated uncertainty is based on generic data.

The next event in the tree "Level Control or No Excess TBP" models different ways that the evaporative cooling criteria for TBP to aqueous mass ratio or TBP layer thickness are violated. The heading represents either the success (or failure) of level control or the probability that a flushing out action is completed (or not completed) properly or it is not missed (or missed) as shown in the fault tree for this top event in Figure A-3.

The probability that the vessels are not flushed out at the end of the six-month interval is conservatively assumed to cause an unavailability of evaporative cooling for six months when the next flushing out is scheduled. The fault tree for this is shown in Figure A-5 based on human error probability to carry out an action. The failure probability/unavailability for level controls is estimated through standard fault tree methodology. The fault tree for the two-train level control system is displayed in Figure A-4. The level transmitters KPC-LT-2000A/B and low level controllers KPC-LLC-2000A/B will close KPC-AOV-2003A/B to terminate the HWS. Standard fault tree modeling is used to also evaluate the possibility of operating at low level when the vessel is heated.

The "venting" heading represents the success of venting to ensure that the evaporative cooling strategy is successful and the solution temperature is maintained below 122°C (251.6°F) to prevent the ROE. Venting is provided by a two-train system consisting of fans and HEPA filters with an additional fan as standby. One fan and one bank of HEPA filters are sufficient to ensure success of the venting strategy. The fault tree model used to evaluate the venting failure probability and the associated uncertainties are shown in Figure A-6. The operation of vacuum pump and the success of condenser cooling are assumed not to be required to ensure the venting and neither of which is credited in the current PRA model. An open venting path, an operational exhaust fan and non-restricted

Loss of temperature control or HX tube rupture at EV2000	Level control or no excessive TBP	Venting system of evaporator		
LOSTC_EV2000	LC_NETBP	VENTING	#	END-STATE-NAMES
			<p>1 OK</p> <p>2 ROE-EV2000-1-NC</p> <p>3 ROE-EV2000-2-NC</p>	

Figure 6-1. The event tree for ROE in EV2000 due to failure of evaporative cooling under normal TBP accumulation condition

flow through HEPA filters are all that is needed to ensure the venting requirement for evaporative cooling. As an example, no vacuum is required for evaporative cooling since all the related criteria are based on azeotropic temperature at atmospheric pressure. Establishing vacuum and cooling the discharged vapor is important for operation of EV 2000, but not necessary for evaporative cooling.

In the fault tree modeling of the EV2000 scenario, it is assumed that individual trains of a two-train control system are physically independent of each other, i.e., the two trains have their own sensors, transmitters, controllers, and actuators, and do not cross-feed or cross check each other (i.e. no system interactions were assumed).

The mission time considered for evaporative cooling is assumed to be 24 hours. Therefore, the mission time or the time required for venting to be operational post initiation of evaporative cooling is assumed to be 24 hours. For example, if the running fans fail after the initiation of evaporative cooling, the standby fan starts and needs to operate for 24 hours for venting to be considered successful.

There is one embedded assumption in developing this event tree. The loss of the super heated hot water temperature control by itself can not generate sufficient heat to fail evaporative cooling if no other failures occur. It should be noted that according to ISA the evaporative cooling could fail if the solution temperature exceeds 122°C (251.6°F). Since the azeotropic temperature at 100 mm-Hg for nitric acid-water solution is about 72°C (161.6°F), the solution temperature of 122°C (251.6°F) is not expected to be achieved unless significant external heating through the heat exchanger by super heated hot water is in effect. The super heated hot water is achieved by electrical heating and it is controlled for a maximum temperature of 122°C (251.6°F). To achieve a solution temperature of 122°C (251.6°F) [in contrast to hot water temperature of 122°C (251.6°F)], the hot water temperature should be significantly higher. Even with loss of temperature control, the capacity of the heating coils would be limited and it is further likely to be controlled by an over-current protection device. In this study, we therefore have assumed that for EV-2000, the evaporative cooling would be successful and the solution temperature could not exceed 122°C (251.6°F) unless both the hot water temperature control is lost and the heat exchanger tubes are ruptured. This event is judged to be unlikely since failures in the hot water temperature control would be readily detectable.

6.4.2.2 ROE in EV2000 for TBP Accumulation under Upset Condition

As discussed earlier, a severe process malfunction resulting in transfer of a large volume of solvent is considered for TBP accumulation under upset conditions. The malfunctions could include failure to maintain the interface level between the aqueous and organics phases, as well as due to such phenomena as the formation of an emulsion, third phase formation, and phase inversion in pulse columns. Such a rapid accumulation of TBP, even though the exact amount is not known, is referred to as upset TBP accumulation.

For addressing TBP accumulation during the upset condition, the TBP transfer path beginning from the source vessel where solvent is introduced to the destination vessel should be identified. This is shown in Figure 6-2. The major barriers in each of the transfer path are discussed below:

Path-1 begins with KPA-PULSE2000 which could inadvertently transfer TBP in an upset condition to KPC-TK1000 through KPA-TK9100. Path-2 starts from KPA-PULSE3200 through KPA-TK9500 and again through KPA-TK9100 to KPC-TK1000. The path between the KPA-TK9100 to KPC-EV2000 via KPC TK 1000 is common to both TBP transfer paths. The following Section describes the barriers to detection of TBP transfer under upset condition.

6.4.2.3 EV2000 Barriers against TBP Accumulation under Upset Condition

KPA-PULSE 2000 & 3200

For the purpose of this study and consistent with the previous BNL study [6-2], a frequency of one per year is assigned to a major malfunction of the aqueous-organic (A/O) normal process inter-phase level control. While the amount of TBP transfer is assumed not to be known, it is assumed that it would be sufficient to violate the conditions on aqueous-to-TBP mass ratio and maximum TBP layer depth necessary to satisfy the evaporative cooling criteria for prevention of ROE. The amount of TBP is controlled by the maximum in/out flows and other plant procedures. A more precise estimate of the TBP quantity inadvertently transferred during such scenarios could provide additional insights for consequence analysis and for developing the timings associated with the accident scenarios.

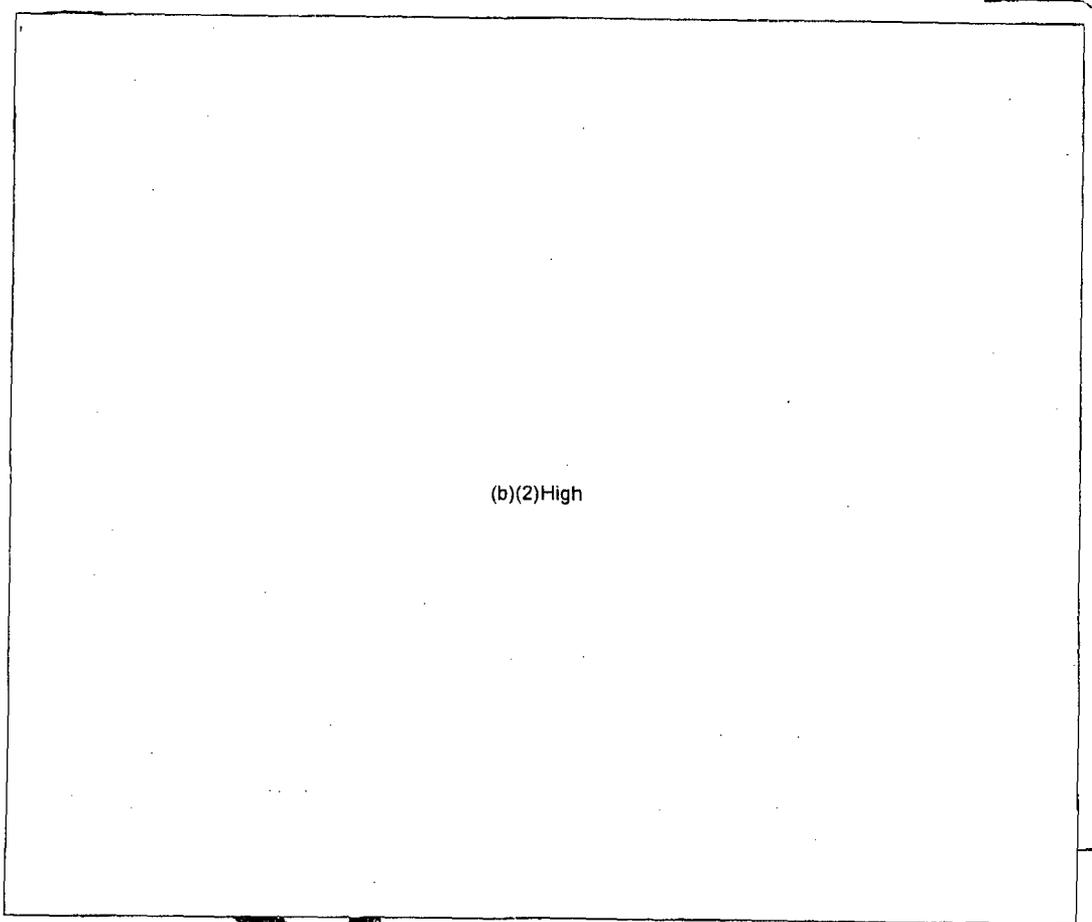
There are some embedded normal process controls and operational strategies that could limit the amount of transferred TBP under the upset condition which are not credited as a part of this study. The normal process control is devised for pulse columns which control the A/O inter-phase level. Aqueous flow is normally continuous. If the aqueous flow stops (for example, due to failure of an air lift) the maximum drawn-off flow would be controlled below 19.2 l/h which limits the amount of organics that can be transferred before the anomaly is detected.

KPA-PULSE 2100& 3100

The diluents washing pulse columns operate in a continuous aqueous phase feed. As discussed above in section 5.3.1 of Chapter 5, these columns are designed to extract dissolved TBP and other organics from the aqueous phase into the hydrocarbon diluent to reduce the probability that organics could migrate to downstream equipment. These pulse columns could also be effective in breaking up the organics entrained by the aqueous phase and reduce the potential of separate phase TBP transfer. They are also equipped with a density measurement device in the disengaging zone as a part of normal process control.

The effectiveness of the diluents washing pulse columns in breaking up the organics and the effectiveness of the normal process density controls in timely detection of the low density organics in the disengaging zone is not currently known. Furthermore, there is no IROFS associated with these columns.

This study has conservatively assigned a 75% probability that the diluents washing columns would be effective in either breaking up any organics entrained in the aqueous phase or inducing a manual termination of TBP transfer¹.



(b)(2)High

Ex 2
High

KPA-TK9100

Sampling is performed on KPA -TK9100 for detection of the TBP. The sampling is done every 75 hours and would include two samples for each sampling batch. The entire group of components that support sampling are considered as IROFS. These are provided in Table 6-4 below.

Standard fault tree modeling to evaluate the failure probability of sampling was developed in this study. This is displayed in Figure A-10. Given sampling failure, the downstream vessels were assumed to be exposed to potential TBP transfer for a maximum mission time of 75 hours before the next sampling activities take place.

¹ This is based partly on the soluble TBP extraction efficiency of about 80% estimated for PULS 2100 functioning in section 5.3.1).

Table 6-4. IROFS for KPA-TK9100-SMPT9100.

KPA-FI9120	Air flow indicator
KPA-FSL-9120	Low flow Switch
KPA-LT-9100	Level instrumentation
KPA-FSL-9100	Sparging air flow (low sparging air flow switch)
KPA-FI-9100	Sparging air flow indicator
KPA-AOV9140A	AOV control to close transfer to down stream tank
KPA-AOV9140B	
KPA-HS9140A	Hand switch permissive
KPA-HS9140B	

KPA-TK9500

Density is measured and controlled in KPA-TK9500 to ensure that organic is not transferred downstream. At a low density threshold, the low density transmitters KPA-DT9501 A/B and the low density controllers KPA-DLC9501A/B will signal the KPA-AOV9510A/B and KPA-AOV9540A/B to close. Closure of these AOVs (in series) will stop the air flow to air lift KPA-AL9510 and KPA-AL9540.

Standard fault tree modeling was used to evaluate the reliability of these protection schemes as shown in Figure A-15. Failure of these protection schemes was assumed to expose the system to the potential risk from ROE for a maximum period of six months (semi-annual flushing out) if the increased amount of accumulated TBP is not detected by sampling in Tank 9100. Since the sampling in Tank 9100 is done every 75 hours, the six month exposure time would be limited to 75 hours for most cases unless sampling is not performed correctly for over six months. Such persistent sampling faults could only occur due to hidden failures in instrumentations/analyzers used for the sample analyses and they are expected to be unlikely. The 75 hour exposure time was considered for the purposes of modeling the scenario.

KPC-TK1000

Density control is available at KPC-TK1000. The purpose of these density monitor loops in KPC-TK1000 is to detect HPT (not TBP). However, they are set at a threshold of 0.9 kg/liter. The density of HPT is 0.77 kg/l. The density of an equal parts mixture of HPT+TBP is about 0.87 kg/liter. According to plant information, the uncertainty associated with the density monitor is +/- 3%. Since the density of HPT+TBP is barely within the tolerance bound of the measurements, it seems that density control at KPC-TK1000 cannot be fully credited for detection of TBP.

In the current PRA modeling, the density control at TK-1000 is partially credited to ensure organic is not transferred downstream to either KPC-TK1500 or KWD-TK4020 through steam jets. At a low density threshold (0.9 kg/l), the low density transmitters KPC-DT1000 A/B and the low density controllers KPC-DLC1000A/B will signal the SPS-AOV2675A/B, SPS-AOV2676A/B, and SPS-AOV2697A/B to close. Closure of any of the SPS-AOV2697A/B (in series) is assumed to terminate the transfer from Tank 1000 to KPC-TK1500 and KWD-TK-4020. The closure of any valve in any of the other sets of valves would terminate the steam jet transfer to the tank associated with that valve.

Standard fault tree modeling is used to evaluate the reliability of these protection schemes shown in Figure A-11. Failure of these protection schemes is assumed to expose the system to the potential risk from ROE for a maximum period of six months (semi-annual flushing out) if the increased amount of accumulated TBP is not detected by sampling in Tank 9100. Since the sampling in Tank 9100 is done every 75 hours, the six month exposure time would be limited to 75 hours for most cases unless sampling is not performed correctly for over six months. Such persistent sampling faults could only occur due to hidden failures in instrumentations/analyzers used for the sample analyses and they are expected to be unlikely. The 75 hour exposure time is considered for the purpose of modeling the scenario.

6.4.2.4 ROE Event Trees in EV2000 for TBP Accumulation under Upset Condition

The effective criteria for evaporative cooling require that the conditions of aqueous to TBO mass ratio of 1:1 and the maximum height of TBP layer of 34 cm be maintained at all times. Accumulation of TBP in downstream vessels, due to failures of controls that are an essential element of the prevention strategy, are assumed to result in a violation of the basic criteria for success of evaporative cooling. Hence, unlike in the previous normal accumulation case, the success of venting is not relevant to prevent a ROE from occurring; adequate venting design is ultimately based on the criterion for the heat of reaction and amount of gases evolved that are a function of the (threshold) amount of TBP present per unit vent area. If the amount of TBP present exceeds the threshold, venting will not prevent ROE via the evaporative cooling strategy. The initiating event for this scenario is the same as considered earlier, i.e., the loss of temperature control in the HWS or rupture of HWS heat exchanger tubes.

Figures 6-3 and 6-4 represent the event trees associated with the transfer of separated phase of organics to EV 2000 from malfunctions in pulse 2000 and pulse 3200, respectively.

Loss of temperature control or HX tube rupture at EV2000	Malfunction at or before KPA Pulse2000	Diluents wash at KPA Pulse2100	Sampling at KPA TK9100 every 75 hours	Density control at TK1000		END-STATE-NAMES
LOSTC_EV2000	MF_PLSE2000	DW_PULSE2100	SPL_TK9100	DST_TK1000	#	
					1	OK
					2	OK
					3	OK
					4	OK
					5	ROE-EV2000-75HRPULSE2000

Figure 6-3. The event tree for ROE initiated from pulse 2000 (Non-OK end-states will lead to separate phase of organic).

Loss of temperature control or HX tube rupture at EV 2000	Malfunction at or before KPA Pulse 3200	Diluents wash at KPA Pulse 3100	Density control at KPA TK9500	Sampling at KPA TK9100 every 75 hours	Density control at KPC TK1000		END-STATE-NAMES	
LOSTC_EV2000	MF_PLSE3200	DW_PULSE3100	DST_TK9500	SPL_TK9100	DST_TK1000	#		
							1	OK
							2	OK
							3	OK
							4	OK
							5	OK
							6	ROE-EV2000-75HRPULSE3200

Figure 6-4. The event tree for ROE initiated from pulse 3200 (Non-OK end-states will lead to separate phase of organic)

Because TK-9100 is common in the two pathways shown in Figure 6-2, the maximum exposure time of the downstream components to the undesired TBP transfer becomes 75 hours. Flushing out the container every six months can thus be neglected in the study.

The end state of the event trees shown in Figures 6-3 and 6-4 denoted by ROE-EV2000-75HR-PULSE2000 and ROE-EV2000-75HR-PULSE3200 represents the annual probability (or frequency) that the separated organic is transported to EV 2000 and the maximum exposure time for such transfer before it can be corrected. These two numbers are translated into unavailability by multiplying the frequency by the exposure period divided by one year. These two end states reflect the fact that if there is a separate organics phase, sampling every 75 hours is the last barrier to the organics entering EV2000 and producing ROE. This assumption is conservative since some of the failure modes in the upstream density monitor instrumentations and controllers of EV2000 could be recognized by the fault detection logic.

The total probability that separated organics are present in EV 2000 at any time then is calculated by simply adding the two unavailability values. The definition and modeling approach for each of the top events in the event tree are listed below:

1. Malfunction at or before pulse 2000

This event tree heading relates to operational malfunction causing the separated phase organics to be transported downstream into the vessels where normally they should not have gone. Per a small amount of empirical evidence, this event is expected to occur with a frequency of about 1 per year. This estimate was constructed on a weak empirical basis, therefore it is expected to be uncertain. For the purpose of this analysis, the estimated frequency was assumed to be lognormally distributed with an error factor of 3.

2. Diluents wash pulse 2100

This heading represents the success of the wash column to break up the separated organic layer transported as a result of operational malfunction. There is currently no empirical data to support a formal estimate of the failure of the wash column to break up the separated organic layer. A subjective failure probability with a mean of 0.25 and error factor of 3 was assigned assuming a lognormal distribution.

3. Sampling TK-9100

This heading represents the success of the sampling of the content of the tank TK-9100 to detect the unacceptable concentration of TBP, thereby isolating further transfer and initiating the flushing out process. The detailed sampling procedure was modeled through standard fault tree analysis and human error evaluation. Since sampling is conducted every 75 hours, failure of a sampling would expose the vessel downstream for a maximum period of 75 hours. Consistent with the standard estimates of the expected values of accident

frequency, one half of this period was used as the fault exposure time for all the downstream vessels.

4. Density TK-1000

This heading represents the partial success of the density monitors in tank-1000 to detect the low density threshold representing the existence of high concentration of HPT instead of TBP. Upon detection, the transfer would be stopped and the content of the tank would be flushed out. The failure probability of the density monitors and the associated controllers will be estimated through formal fault tree methodology.

5. Malfunction at or before pulse 3200

This event tree heading relates to operational malfunction causing the separated phase organics to be transported downstream into the vessels where normally they should not have gone. Per a small amount of empirical evidence, this event is expected to occur with a frequency of about 1 per year. This estimate was constructed on a weak empirical basis therefore it is expected to be uncertain. For the purpose of this analysis, the estimated frequency was assumed to be lognormally distributed with an error factor of 3.

6. Diluents wash pulse 3100

This heading represents the success of the wash column to break up the separated organic layer transported as a result of operational malfunction. There is currently no empirical data to support a formal estimate of the failure of wash column to break up the separated organic layer. A subjective failure probability with a mean of 0.25 and error factor of 3 was assigned assuming lognormal distribution.

7. Density TK-9500

This heading represents the success of the density monitors in tank-9500 to detect the low density threshold representing the existence of high concentration of organics. Upon detection, the transfer would be stopped and the content of the tank would be flushed out. The failure probability of the density monitors and the associated controllers will be estimated through formal fault tree methodology. Failure of the density monitor in Tank 9500 would allow the high concentration of organics to be transported to TK1000.

8. Loss of Temperature control or Heat Exchanger Tube Rupture

This heading acts as a traditional initiating event in PRAs representing various ways that the solution temperature in EV 2000 could increase such that ROE could be initiated if evaporative cooling strategy is not successful. This could occur due to loss of temperature control in Hot Water System or heat exchanger tube rupture.

The standard fault tree model of a two-train temperature control system composed of KPC-TE2003 A/B, KPC-TT2203 A/B, and controllers

KPC-THC2003A/B which signal the closure of KPC-AOV2003A/B are utilized for estimating the frequency for loss of temperature control. This was described earlier under normal TBP accumulation and the associated fault tree is shown in Figure A-2. The frequency associated with heat exchanger tube rupture and its associated uncertainty was obtained from generic data.

Similar to the case for normal accumulation, the temperature control failure of the super heated hot water by itself can not generate sufficient heat to fail evaporative cooling if no other failures occur. It should be noted that according to ISA the evaporative cooling could fail if the solution temperature exceeds 122°C (251.6°F). Since the azeotrope temperature at 100 mm-Hg for nitric acid is about 72°C (161.6°F), the solution temperature of 122°C (251.6°F) is not expected to be achieved unless significant external heating through the heat exchanger by super heated hot water is in effect. The super heated hot water is achieved by electrical heating and it is controlled for a maximum temperature of 122°C (251.6°F). To achieve a solution temperature of 122°C (251.6°F) [in contrast to hot water temperature of 122°C (251.6°F)], the hot water temperature should be significantly higher. Even with loss of temperature control, the capacity of the heating coils would be limited and it is further likely to be controlled by the over-current protection device. In this study we therefore have assumed that for EV-2000, the evaporative cooling would be successful and the solution temperature could not exceed 122°C (251.6°F) unless both the hot water temperature control is lost and the heat exchanger tubes are ruptured. This event is assumed to be unlikely since failures in hot water temperature control would be readily detectable.

9. Venting

Under TBP accumulation in an upset condition, the venting at EV2000 does not prevent ROE from occurring as discussed earlier. It is effective only under normal conditions, as discussed in Section 6.4.2.1.

In the fault tree modeling of the EV2000 scenario, it is assumed that individual trains of a two-train control system are physically independent of each other, (i.e., the two trains have their own sensors, transmitters, controllers, and actuators), and do not cross-feed or cross check each other (i.e. no system interactions were assumed). For the venting system, it is also assumed that the mission times of the running fans are 24 hours considering the availability of the (third) standby fan.

The frequency of the initiating event in EV 2000, i.e., loss of temperature control or heat exchanger tube rupture, for all scenarios is about 2.2E-03 per year. Based on the frequency of flushing out, the fault exposure times of basic events are all six months. However, in the Upset Condition case, for those scenarios that involve failure in the density control at TK1000, the fault exposure times are 75 hours since TK1000 is downstream of TK9100 where the sampling is performed every 75 hours. It is assumed that it would take approximately 30 minutes to analyze the samples at TK9100. The mission time, i.e., the period post initiator where the evaporative cooling should continue successfully, is considered to be 24 hours.

The frequencies of the ROE sequences under both normal and upset conditions are summarized in Table 6-5.

Table 6-5. Frequency of ROE at EV2000.

Sequences	ROE-EV2000-75HR-PUL2000 (Upset Condition) /year	ROE-EV2000-75HR-PUL3000 (Upset Condition)/year	ROE-EV2000-1-NC (Normal Condition) /year	ROE-EV2000-2-NC (Normal Condition)/year
ROE Frequencies	1.6E-08	6.5E-11	5.8E-06	5.5E-06

An uncertainty analysis was performed for all of the ROE sequences for EV2000 scenarios using the Monte Carlo simulation provided in SAPHIRE. This is shown in Table 6-6, where point estimates of the sequence frequencies and the 5th and 95th percentiles are presented in Columns 2–4. In addition, the dominant cutsets for each ROE sequence are presented in Column 5.

In the case of ROE at EV 2000 under the upset condition, the point estimates of the frequency are low, demonstrating the relative robustness of the TBP prevention strategy designed to prevent TBP from migrating to vessels it is not supposed to go to. The dominant cutset in this scenario is the failure of density control at tank TK 1000 to stop organics from entering the evaporator EV 2000.

In the case of ROE at EV 2000 under the normal condition and failure of evaporative cooling, the dominant cutset in one sequence is the plugging of both sets of HEPA filters; in the other it is the failure to flush out the system after six months.

DRAFT

Table 6-6. Summary of ROE Sequences of EV2000 Scenarios.

Sequences	Point Estimate Frequency per Year	5 th percentile (per year)	95 th percentile (per year)	Main Contributors (dominant cutsets)
ROE-EV2000-75HR-PUL2000	1.6E-08	4.6E-10	5.8E-08	DENSITY-CTRL-VALID (Ineffectiveness of density control at TK1000) KCA-FET-SAMP-X-OP-FOP (fraction of time sampling failed between successive sampling intervals) KPA-PDW-2100-X-OP-FOP (Failure of diluent wash at pulse 2100) KPA-PUL-2000-X-OP-FOP (Malfunction of KPA pulse 2000)
ROE-EV2000-75HR-PUL3000	6.5E-11	1.1E-12	3.4E-10	DENSITY-CTRL-VALID (Ineffectiveness of density control at TK1000) KPA-DTX-9501-X-OP-CCF (CCF of density transmitter KPA-DT9501A/B), KPA-LAB-ALYS-1-OP-FOP (Failure of analysis of samples at TK9100) KPA-PDW-3100-X-OP-FOP (Failure of diluent wash at pulse 3100) KPA-PUL-3200-X-OP-FOP (Malfunction of Pulse 3200)
ROE-EV2000-1-NC	5.8E-06	2.3E-07	3.0E-05	KPC-HEP-PLUG-X-OP-CF2 (CCF of plugging of the two sets of HEPA filters)
ROE-EV2000-2-NC	5.5E-06	8.8E-07	1.9E-05	FLUSHING-OUT-FAILURE (Failure to flush out every six months)

6.5 Red Oil Scenario for KPC-TK 3000

Concentrates from KPC-EV2000, the first evaporator, are drawn off several times a day at a constant rate by an airlift and they are sent to KPC-TK 3000. Another airlift operates continuously to prevent stagnation and cooling of the liquid at the bottom of the draw-off system between concentrate draw-offs, thereby minimizing the risk of clogging. The concentrates containing impurities that are collected in KPC-TK3000, the concentrates collecting tank, are transferred to the High Alpha Liquid Waste area of the KWD unit or recycled back to the main feeding tank.

The concentrates are cooled in tank TK3000 which is fitted with a cooling water loop. This 500 L tank is also fitted with a scavenging air inlet and a decontamination spray pipe fed by steam jet J3400. It has a buffer capacity of about 15 days for the PDCF

period operations and about 7 days for the AFS period operations. In order to avoid the formation of sodium nitrate precipitate in tank TK3000 during treatment of solution with high salinity (AFS period), an acid flush-out is normally carried out after massive draw off from EV 2000. The KPC-TK 3000 operates normally at a temperature around 40°C. The red oil prevention strategy applied to KPC-TK3000 is evaporative cooling. If the temperature reaches a set point of 80°C (176°F), steam jets will be shut off, and the solution volume is verified and maintained at least at 42 liters to ensure that the evaporative cooling would be successful. Semi-annual flushing ensures that the amount of TBP is limited to 21 liters in the tank.

6.5.1 Conditions Necessary for Red Oil Explosion in TK 3000

The following two conditions are necessary for a viable ROE scenario to occur:

1. A rising tank temperature to 80°C (176°F) due to failure or degradation of the tank cooling/mixing system.
2. Failure of evaporative cooling.

The necessary conditions for successful evaporative cooling as noted in the ISA Summary are provided below. Failure of evaporative cooling is assumed if one or more of the following conditions are not met:

- Minimum water-to-TBP mass ratio of 1:1
- Maximum TBP layer depth of 34 centimeters (cm)
- Maximum process solution temperature of 122°C (251.6°F)
- Open (adequately vented) system

Two cases were considered: in one case the tank contents are well mixed and in the other case a separate phase (layer) of TBP is formed. The evaporative cooling for the latter case would be similar to what was discussed for the red oil scenarios in KPC-EV2000 considering that the layer thickness would be much smaller in the tank due to larger tank diameter compared to the evaporators. It is therefore not repeated here.

For a homogenized mixture, the solution temperature would increase to the boiling temperature of water first. As some of the water boils off, the boiling temperature of water and nitric acid mixture would increase. The trend would continue up to the point where the azeotropic limit of nitric acid-water is reached (boiling point of 122°C [251.6°F]). The homogenized mixture of nitric acid, water, and TBP should satisfy the 1 to 1 aqueous to TBP mass ratio criteria. This can be verified through the tank level indication since the maximum TBP amount would be limited to 21 liters. If the operator determines that a sufficient level is not maintained, additional injection of aqueous feed will be commenced using decontamination water spray. It should be noted that the operator is directed to isolate the external heat sources by shutting KPC J3400 & KPC-AL2100, and to verify the tank level when the temperature reaches 80°C (176°F) and to take the proper action and not wait until temperature reaches 122°C (251.6°F).

A demand for evaporative cooling would become necessary when the temperature of the tank content increases to 80°C (176°F) from 40°C (104°F). Various failures that could raise the tank temperature are discussed below.

6.5.2 Conditions that Could Result in Excessive Tank Temperature Rise

Tank TK 3000 receives the concentrate from Evaporator 2000 and cools it. The draw off of the concentrates depends on the feed cycle. Tank 3000 has a buffer capacity of 15 days for the PDCF cycle and 7 days for the AFS cycle. For the AFS cycle, the draw off of EV 2000 is done in batches. One batch cycle typically takes at least 5 days which includes 84.5 hours for the concentrate phase, 2.3 hours for the acidic flush out, 8 hours for massive drawing off, and 24 hours for filling up and heating EV 2000. The tank content therefore varies depending on the feed, but bounding content compositions for the tank heat up upon loss of cooling are Pu (7.7 kg or 15.4 g/L), U (7.6kg or 15.2 g/L), U²³⁵ (2.3 kg or about 4.6 g/L), Am (1.566kg or 3.1 g/L), TBP (maximum amount of 21 liters), and nitric acid (~ 9.4 N).

The tank's conditions are amenable to ROE if the temperature is raised sufficiently and evaporative cooling is not effective. The contents of Tank 3000 are normally cooled. The tank is also equipped with a spray system to ensure proper mixing thereby minimizing the difference between the bulk and the local temperatures. The tank content is composed of radioactive material with a high alpha radiation (e.g., Am). The tank contents are sampled routinely (approximately once every five days to monitor the various radio nuclides).

The major heat sources inside the tank are: slow chemical reactions and radioactive decay resulting in alpha and beta emissions. The major heat removal mechanisms which are facilitated by mixing of the tank contents are the tank cooling system, and the HVAC system. Based on review of various licensee documents, the following assumptions were made for the purpose of PRA modeling.

Under normal process conditions, failure of room HVAC (Cell 140) by itself is not expected to result in excessive tank heat up and initiation of evaporative cooling. This appears to be consistent with the operating philosophy of the facility for loss of HVAC. If loss of HVAC occurs, the KPC unit will be shutdown and the tank inlets/outlets will be isolated. In such cases, it appears that the tank cooling is relied on for stable tank condition. This assumption is also consistent with other similar tanks since the additional heat generated by radioactive decay (alpha and beta emission) is small, about 171 W.

Well mixed tank content appears to be necessary due to the following reasons:

- Help preventing sodium nitrate from solidifying in AFS cycle,
- Preventing the creation of a separate TBP phase in the tank, and
- Preventing the potential for hot spots and increased TBP-nitric acid reaction, which, if not prevented, could generate heat in excess of the normal heat removal capability provided by the cooling coils and cell HVAC.

We therefore consider conservatively that the failure of mixing could result in local hot temperature spots, which could result in an increase of temperature in the tank's contents (the initiating event for ROE scenario for evaporative cooling).

The same assumption, i.e., not requiring cell HVAC used for normal process control, are also considered valid for the case when mixing has failed.

In summary, the following assumptions are used for the PRA analysis:

1. Failure to provide cooling flow to the tank heat exchanger is assumed to be sufficient to result in tank heat up and initiation of evaporative cooling. However, failure of HVAC system is assumed to result in shutdown of KPC unit but not initiation of evaporative cooling. Therefore, the failure of HVAC is not modeled in PRA.
2. Failure of spray mixing is assumed to create hot spots inside the tank where accelerated chemical reactions could take place resulting in further heat up of the tank content, chemical degradation of TBP, and initiation of evaporative cooling.
3. Increased amount of TBP inside the tank due to inadvertent transfer would increase the exothermic chemical reactions. The increased heat generation is assumed not to be able to increase the temperature of the tank content sufficiently to cause ROE if all other cooling systems are available. However, upon failure of the cooling or the mixing system when the evaporative cooling would be necessary, it is assumed not to be effective due to increased amount of TBP, which would impact the aqueous to TBP mass ratio and TBP layer height.

6.5.3 ROE Event Tree for KPC-TK 3000

The event tree for ROE scenarios for KPC-TK 3000 is provided in Figure 6-5. The headings for various event tree branches are discussed below.

Loss of Cooling or Mixing in KPC-TK 3000:

This heading is considered as the initiating event for this event tree. The initiating event frequency normally is estimated from historical data; however, due to lack of historical data, it is estimated based on fault tree evaluation of the systems involved. The initiating event is assumed to occur either due to failure of the cooling system for KPC-TK 3000 or the mixing spray. Such failures, if they occur, are assumed not to be recoverable; i.e., they are assumed not to be restored before the temperature of the tank content reaches 80°C and evaporative cooling is initiated. The major support systems that are required for operation of these systems were identified for the purpose of the fault tree modeling. The cooling water system cools CND 2200, CND 2800, COOL 2900 for EV 2000, and also provides cooling to the cooling coils of Tank 3000. Upon loss of the cooling water system, the KPC unit will be shutdown (all vessels isolated). Low flow in cooling water is indicated through FI3000. Potential leakage of the cooling coil to the tank should be detected through high tank level warning. The system responsible for mixing is the service air or scavenging air. The scavenging air flow rate and low flow warning and alarms are provided through FI 3001, and FWL 3001. The HVAC system depends on the electrical power and chilled water systems; however, it is not modeled here due to the reasons discussed earlier.

No Transfer of Separate Organics:

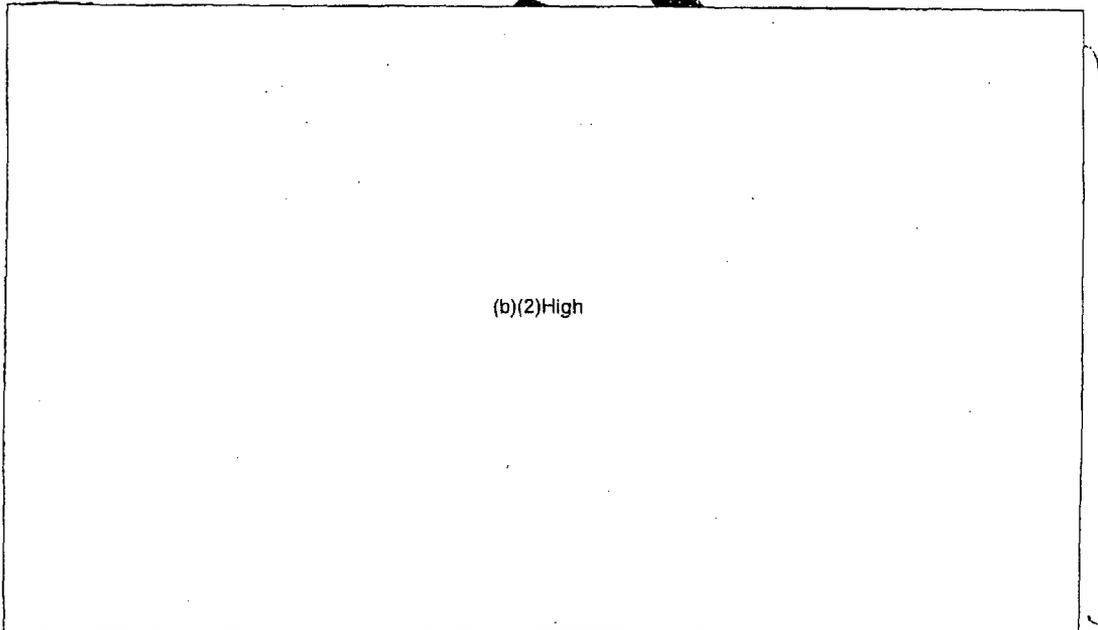
This branch of the event tree is estimated similar to what was discussed for the Section for ROE scenarios for KPC-EV2000. As noted in that section this heading represents the possibility that separate phase TBP is transferred into the KPC unit from the KPA unit

sometime before the occurrence of the initiating event which results in increased temperature of the tank's contents. Due to common pathways for transport of separate phase TBP to various KPC vessels including EV 2000 or TK 3000, the PRA models developed earlier for EV 2000 would be applicable. The probability estimated from these models for excessive organics to be present in KPC-TK 3000 via transfer of separated organic layer from KPA unit is shown as "No Separated Organic" in the event tree heading of Figure 6-1.

Level Control or No excessive TBP:

This heading addresses the operator action required to provide aqueous makeup to ensure an effective evaporative cooling process in response to a temperature alarm. KPC-TK 3000 is equipped with redundant temperature transmitters with alarm which should direct the operator to initiate the evaporative cooling process based on the level in the tank and assuming that the total amount of organics is below 21 liters. The maximum amount of organic is controlled by flushing the KPC unit every six months. Failure to flush out is also considered as a possible failure mechanism for this branch. If the six month flushing is successful, evaporative cooling could still fail due to failure of the temperature transmitters, the aqueous makeup paths, or the required operator actions. All these items are modeled under this event tree branch.

Table 6-7 identifies various tank instrumentations and controllers for KPC-TK3000.



(b)(2)High

EX 2:
High

The system for aqueous make up is decontamination water which is injected through the spray pipe by steam jet J3400. The operation requires an operator action by opening the steam and aqueous valve. Since the content of the TK-3000 gets diluted especially after the massive draw off required for AFS feed (which includes nitrate salts of Na and Ga), there would be ample time available for the operator to perform this action. The evaporative cooling will be initiated upon receipt of a high temperature alarm, and it would require the operator to monitor and maintain the tank level.

Venting

The "venting" heading represents the success of venting to ensure that the evaporative cooling strategy is successful and the solution temperature is maintained below 122 °C (251.6°F) to prevent the ROE. Venting is done through demister 1010 from port P2 as shown in the tank schematic of Figure-6-6. Formal fault tree models are used to evaluate the venting failure probability and the associated uncertainties for this heading.

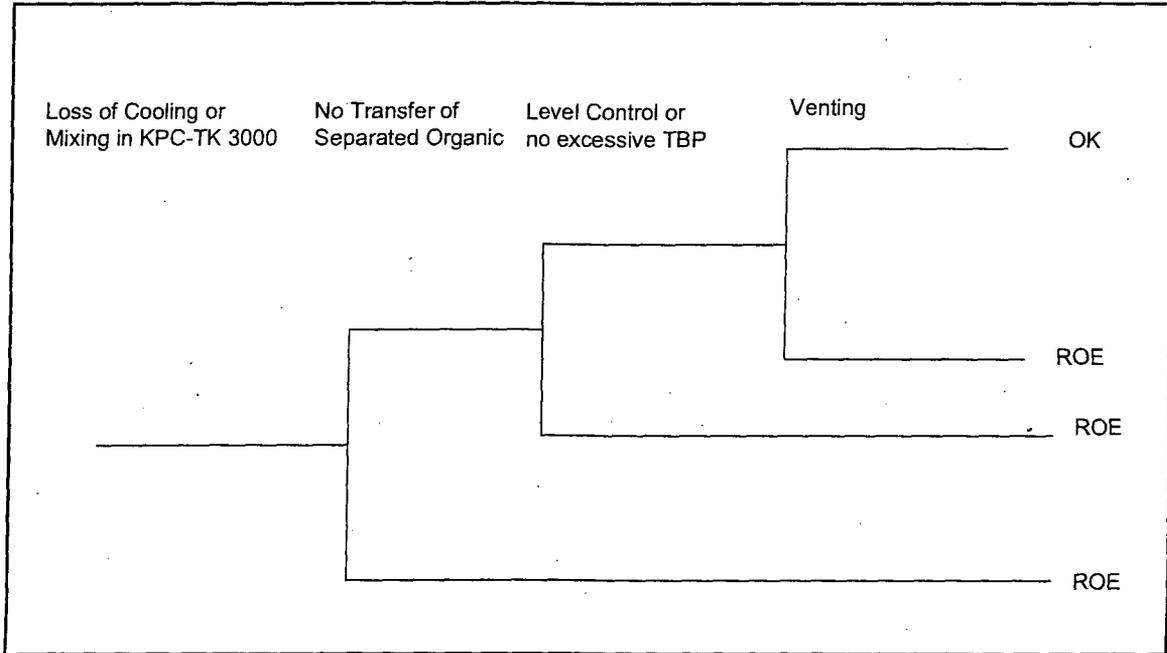


Figure 6-5. Event Tree for ROE for KPC-TK3000.

Official Use Only

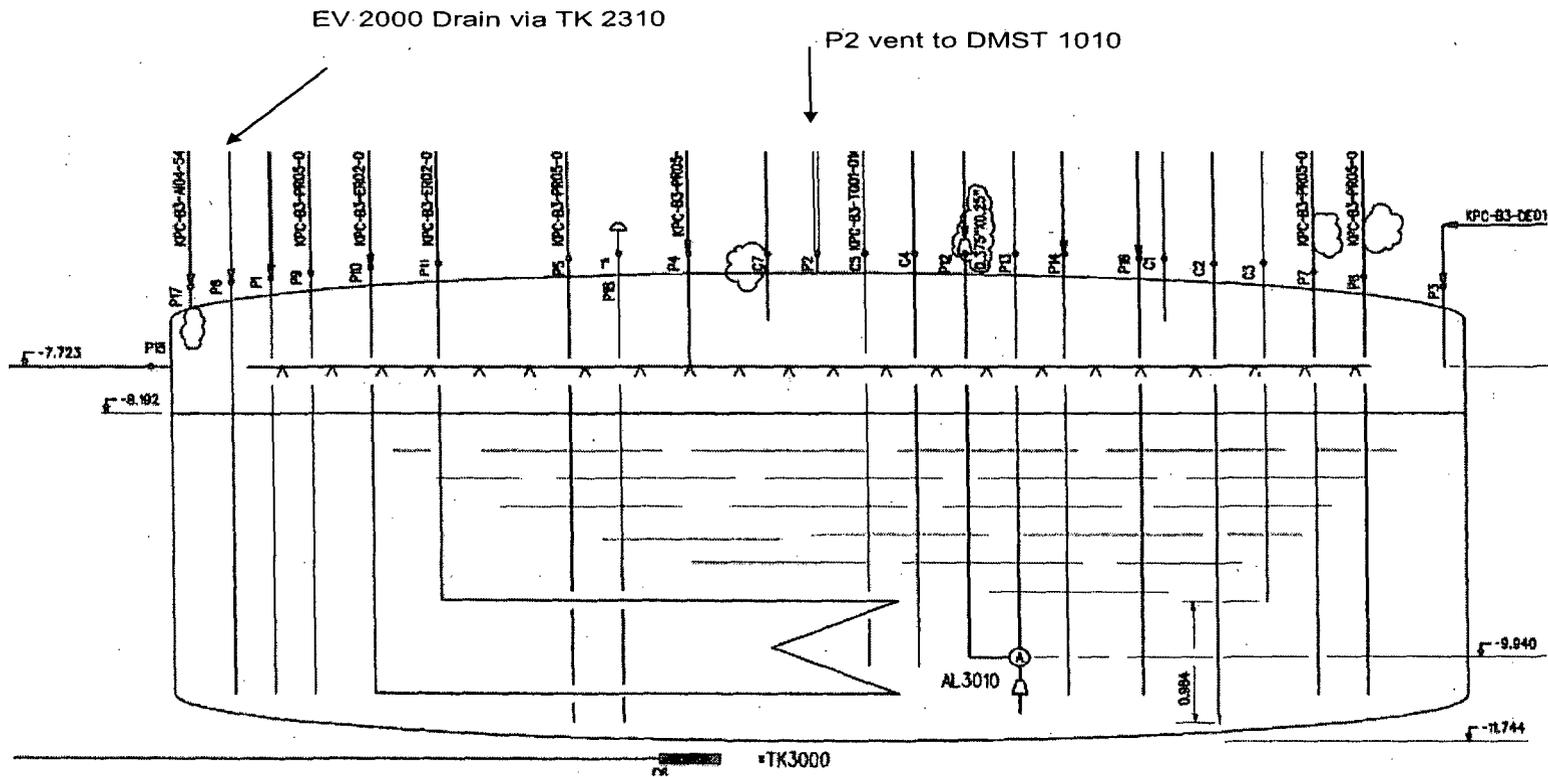


Figure 6-6. Schematic Diagram of KPC-TK3000.

Official Use Only

Table 6-8 shows the point estimate frequency of ROE sequences at TK 3000 under both upset and normal TBP accumulation conditions. The frequency of the initiating event, loss of cooling or mixing in TK 3000, modeled in the fault tree shown in Figure A-17, is about 7.2E-04 per year.

Table 6-8: Frequency of ROE Sequences under Normal and Upset Conditions at TK3000 (Initiating Event Frequency of about 7.2E-04 per year)

Sequences	ROE-TK3000-PUL2000 (Upset Condition)/year	ROE-TK3000-PUL3000 (Upset Condition)/year	ROE-TK3000-1-NC (Normal Condition)/year	ROE-TK3000-2-NC (Normal Condition)/year
ROE Frequencies	5.2E-09	2.2E-11	1.9E-06	2.2E-05

An uncertainty analysis was performed for all of the ROE sequences for the TK 3000 scenarios using Monte Carlo simulation provided in the SAPHIRE code. The results are shown in Table 6-9, which shows the particular ROE sequence, the point estimate frequency, and the 5th and 95th percentile frequencies. The main contributors, i.e., the dominant cutsets, to the sequences are also shown in Table 6-9.

The ROE sequences of TK 3000 that arise from upset conditions, ROE-TK3000-PUL2000 and ROE-TK3000-PUL3000, are caused by malfunctions in the pulse units PULSE 2000 and PULSE 3000. The PRA shows that these sequences have very low frequencies. This demonstrates the robustness of the barriers designed to prevent large amounts of TBP from migrating to unintended vessels. The main contributors to these sequences are failures of density controllers in tank TK 1000 in the acid recovery unit and sampling failures in tank TK 9100 in the KPA unit. Other contributors include common cause failures of density transmitters, and failure of the diluent wash pulse units to remove organics from the aqueous solution phase.

The ROE sequences of TK 3000 under normal accumulation, ROE-TK3000-1-NC and ROE-TK3000-2-NC, derive from the failure of evaporative cooling to remove heat and control the runaway ROE. The dominant cutsets in the former sequence are common cause failures resulting in the plugging of two sets of HEPA filters. In the latter sequence, the dominant cutset is the failure of the operator to recognize the alarm on low level of solution in the tank and take action to add aqueous solution to prevent the progression of the ROE.

Table 6-9. Summary of Uncertainty Analysis for ROE Sequences of TK3000 Scenario.

Sequences	Point Estimate Frequency per Year	5 th percentile	95 th percentile	Main Contributors (dominant cutsets)
ROE-TK3000-PUL2000	5.2E-09	1.5E-10	1.9E-08	DENSITY-CTRL-VALID (Ineffectiveness of density control at TK1000) KPA-LAB-ALYS-1-OP-FOP (Failure of analysis of samples at TK9100) KPA-PDW-2100-X-OP-FOP (Failure of diluent wash at pulse 2100), KPA-PUL-2000-X-OP-FOP (Malfunction of KPA pulse 2000)
ROE-TK3000-PUL3000	2.2E-11	3.4E-13	1.1E-10	DENSITY-CTRL-VALID (Ineffectiveness of density control at TK1000) KPA-DTX-9501-X-OP-CCF (CCF of density transmitter KPA-DT9501A/B), KPA-LAB-ALYS-1-OP-FOP (Failure of analysis of samples at TK9100) KPA-PDW-3100-X-OP-FOP (Failure of diluent wash at pulse 3100) KPA-PUL-3200-X-OP-FOP (Malfunction of Pulse 3200)
ROE-TK3000-1-NC	1.9E-06	6.1E-08	1.0E-05	KWG-HEP-PLUG-X-OP-CF2 (CCF of plugging of the two sets of HEPA filters)
ROE-TK3000-2-NC	2.2E-05	1.1E-05	4.3E-05	KPC-HMN-CONG-X-OP-FOP (Failure of the operator to recognize level alarm)

6.6 Red Oil Scenario for KPC-EV6000

KPC-EV6000 is a natural recirculation thermo-siphon type boiler that utilizes pressurized steam at approximately 2 bar gage and 133°C (271.4°F) as a heating fluid. EV temp is adjusted by controlling the flow of steam. At the high temperature threshold, TT6003A/B sends data to controller THC6003A/B which closes AOV6003A/B to terminate steam flow. The liquid/vapor mixture produced at the top of the evaporator is separated in the separator. The separator is comprised of a capped tray, a coalescing sieve and a demister sieve sprayed continuously with demineralized water. The concentrates from EV 6000 are drawn off discontinuously several times a day at a constant rate utilizing the FIC 6100 and air lift AL6100. The concentrates are cooled by chilled water loops EX6500/EX6501.

Analysis performed by the licensee showed that TBP accumulation will not occur at EV 6000 and CLMN 2500 [Ref. DCS01 KKJ CG CAL H 10866A]. The licensee,

therefore, relied on prevention mechanism that has been constituted to prevent excessive transfer of TBP from KPA to KPC as the only strategy for EV 6000. KPC EV-6000 is equipped with several process monitors that protect the vessel from other hazards and may indirectly help the prevention of ROE in an unlikely event of excessive transport of TBP from KPA to KPC. These instrumentations and controls are noted below in Table 6-10.

(b)(2)High

EX 2
High

Several features can be noted regarding the unit in Table 6-10:

1. The steam side temperature is maintained at 133°C (271.4°F); this implies the solution is maintained around 110°C (249.8°F), which governs the TBP destruction rate.
2. During an upset condition in EV 2000 a scenario could be envisioned that additional TBP could be entrained (steam stripped) and accumulated in the feeding tank to EV 6000 (condensate pot of EV 2000). The increased amount of TBP could establish a separated layer in this feeding tank. Since this feeding tank also provides a vacuum seal between EV 2000 and EV 6000, its level is monitored and maintained. If the separated layer is drained to EV 6000, it would result in loss of vacuum in EV 2000 and subsequent shutdown of the KPC unit. Therefore, only soluble TBP could be fed to EV 6000. Furthermore, the concentrate in EV 6000 is drawn several times a day such that TBP accumulation is unlikely. In addition, the operator could detect the low density via DI-6000.
3. If for some reasons, such as occurrence of a higher vacuum condition, the flow rate in EV 2000 could increase, thereby increasing the amount of TBP that is carried out to EV 6000. Such an increased amount of TBP is unlikely to exceed the TBP destruction rate in EV6000 and furthermore it can not be accumulated because of reasons discussed under item 2 above.

The following conclusion was made based on the previous discussion:

There is a possibility, although unlikely, of an event that transfers large amounts of TBP to KPC tanks/vessels from KPA due to failure of multiple prevention barriers. In case an ROE does not take place in any of these vessels/tanks, there would be a potential for higher than normal TBP in EV 2000 to be carried with the distillate such that the TBP concentration entering EV 6000 significantly increases. Since the distillate is condensed and then drained to EV 6000, the soluble TBP concentration could vary from about 50 mg/liter up to 300 mg/liter (the latter corresponds to the saturated TBP solubility in nitric acid). Considering the nominal flow rate of 30.5 liter/hr, the maximum accumulation of free organic in EV 6000 within 8 hours (assuming only 50 mg/l is destroyed) will be limited to about 61 grams. Frequent draining of EV 6000 and high operating temperature, which is expected to destroy all 300 mg/liter of soluble TBP, will significantly decrease the likelihood of ROE. Transfer of separated phase organic is protected through multiple barriers prior to EV 2000 and the likelihood of separated phase TBP to be established in the condensed distillate and transferred to EV 6000 is judged to be unlikely, since it will result in loss of vacuum in EV 2000 and shutdown of the KPC unit. This scenario is, therefore, not modeled any further quantitatively and it is screened out qualitatively.

6.7 Red Oil Scenario for KCD EV 3000

The oxalic mother liquors, supplied from the feeding tank TK 2000, are concentrated in the natural circulation thermo-siphon evaporator EV 3000. The evaporator includes a boiler used for evaporation of the feed solution and reflux from the rectification column. It has a tubular heat exchanger. The heating fluid (steam) occupies the shell side and the mother liquor to be evaporated circulates in the tubes. Instrumentation is used for measuring the level, density, and temperature. The evaporator also includes a rectification column, which backwashes the steam, rectifies the acid, and decontaminates the distillates.

The evaporator operates at a constant heat input from the secondary steam supplied by a vaporizer (EV 5000). The liquid level in the evaporator measuring tube is regulated by the evaporator feed flow rate. The concentration factor of the oxalic mother liquors is determined by the draw-off rate of the concentrate.

The vaporizer EV 5000 is equipped with diverse IROFS for high temperature and high pressure control (TT5101A and THC5101A) which close the steam valve AOV5300A to the EV 3000 boiler. The normal steam temperature is 130°C (266°F) and it is controlled below 133°C (271.4°F).

The distillates from the rectification column of the evaporator are condensed, cooled to a temperature of approximately 40°C (104°F), and directed downward to a passage pot. From the passage pot, the distillates are supplied via the reflux system to the top of the evaporator at a regulated rate or to the distillate control tank.

6.7.1 Conditions Necessary for ROE

The conditions necessary for ROE in EV 3000 are assumed to be satisfied if a sufficient amount of TBP is present; however, the amount of TBP that enters the evaporator from

the feeding tank TK 2000 is controlled below its solubility limit of 50 mg/liter. This small amount of TBP will be fully and safely reacted in the aggressive environment that exists in this evaporator. The vessel in effect is protected by the prevention strategy. This study conservatively assumes that the ROE could occur if the soluble TBP amount is not controlled or if a separated phase of TBP is transferred to the evaporator.

6.7.2 Potential TBP Transfer Mechanism from KPA to KCD

There are three mechanisms for transferring organics (TBP/HPT) into the KCD evaporator EV 3000. These are as follows:

1. Small quantities of soluble TBP that are transferred when the facility is operating properly. This is considered normal operation and the transferred TBP amount is assumed to be completely and safely destroyed by the aggressive environment in EV 3000. This case is considered safe and not modeled in the PRA.
2. A slow accumulation of small quantities of TBP, such that it eventually creates a separate phase in the KCD evaporator EV 3000 (in excess of what can be destroyed in EV 3000), could occur under certain conditions. TBP/HPT accumulation from KPA is due to transfer of droplets of solvents which are mechanically entrained with the aqueous phase due to improper operation of the pulsed units. Two safety barriers were considered for this scenario. The effectiveness of slab settler 3300 to separate out the entrained TBP/HPT is considered as the first barrier. In the unlikely event that the solvent passes through the KPA slab settler 3300 in such amounts that it could become a separate phase in the KCD evaporator, process sampling is performed upstream in the KCA batch constitution tanks to confirm that the amount of soluble TBP is sufficiently low. Thus, these sample points and the associated administrative IROFS (i.e., vessel isolation, vessel homogenization, sample line purging, sample vial traceability, laboratory sampling process, and communication of results from laboratory to the control room) are considered to ensure that the sample is representative of the contents of the tank. The mixing of tank contents is done by three air lifts and the sampling is done approximately every 3 days (2 samples/batch, and approximately 2.2 batches per week).
3. A severe process malfunction leading to the transfer of a relatively large volume of solvent. There are several different barriers that are designed to prevent such malfunction. As an example, diluent wash KPA-PULSE 3100 is designed and operated such that it removes solvent droplets that are mechanically entrained with the aqueous phase, reduces the amount of TBP dissolved in the aqueous phase, and potentially breaks up any TBP transferred in the form of an emulsion. Third phase formation is also controlled by addition of appropriate chemical agents. Similarly, there are two safety barriers that can be considered for this scenario. The effectiveness of slab settler 3300 to separate out the separate phase TBP/HPT is considered as the first barrier. The process sampling that is performed upstream in the KCA batch constitution tanks to confirm that the amount of soluble TBP is sufficiently low is considered as a second barrier.

There is also a possibility that solvent solution has leaked into the KWG active gallery drip tray and is transferred to a KCD break pot. A preventative safety strategy is utilized by taking IROFS samples in this drip tray to test for the

presence of TBP prior to transfer to KCD. If these samples contain TBP, then the solution is not drained to KCD and would be drained either to the KPA process unit or pumped to a drum for separate treatment.

Figure 6-7 shows the various possible transfer paths of solvent to KCD EV 3000. Safety barriers and the equipment that could help in preventing the solvent from reaching KCD EV 3000 are shown by boxes that have double line boundaries.

The movement of a separate phase of solvent to the KCA unit should not occur, since the KPA unit is designed with both a diluent washing pulse column and a slab settler tank. The slab settler tank is equipped with redundant IROFS density instrumentation and a related administrative control that requires the settler to be preloaded with aqueous liquid. These IROFS are credited for the prevention of moving separate phase solvent to downstream vessels in the KCA and KCD units and, reduce the risk of a solvent explosion event in the heated equipment of these units. Redundant density instrumentation in the settler have also been identified to be IROFS to ensure: (1) the density interface on the settling side of the settler does not drop below the weir height, (2) the settler is not initially filled with the lighter density material, and (3) the lighter material is not sent to the KPA oxidation column. Thus, the combination of the passive design of the KPA slab settler and the active engineered redundant density instrumentation ensure that explosions involving solvent are highly unlikely to occur in the KCA and KCD units due to separate phase solvent.

IROFS controlled samples taken in KCA*TK1000 and KCA*TK2000 not only prevent solvent transfer to downstream vessels in the KCA unit but also prevent transfer to vessels in the KCD unit. These samples are taken with an approximate frequency of 2.2 batches per week and 2 samples per batch, via mixing and through three air lifts. The samples are analyzed for multiple process constituents but specially monitored for TBP and pH. TBP measurements are done with an HPLC analyzer (2 channels per analyzer) and the pH with a pH measurement device.

DRAFT

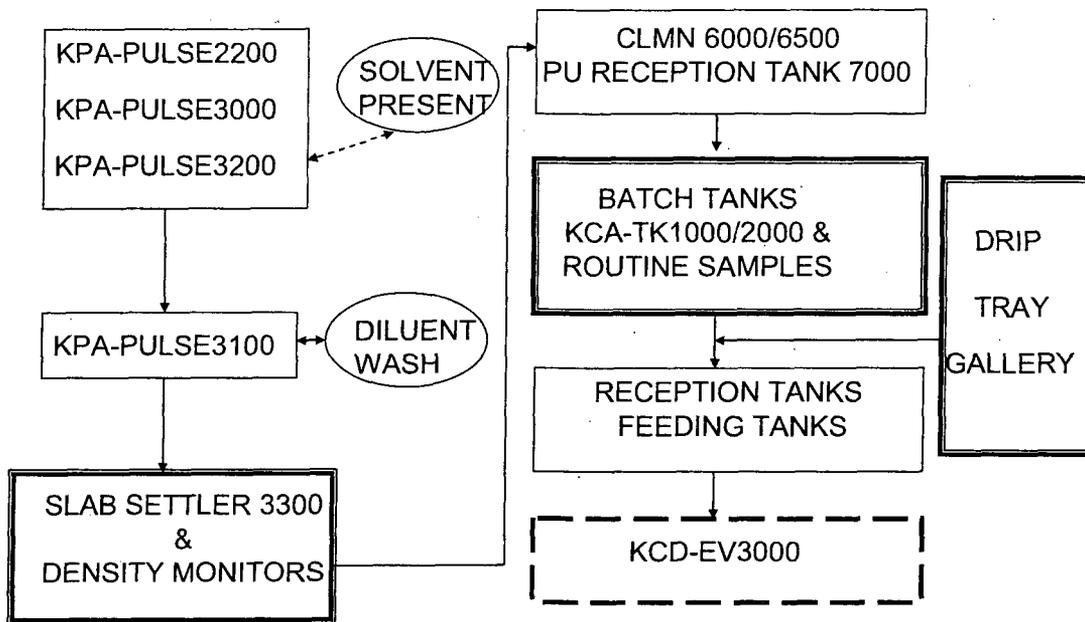


Figure 6-7. The various transfer paths of solvent to KCD-EV 3000 and the associated safety barriers that can be credited

6.7.3 Event Trees for ROE in KCD-EV3000

The event tree for the slow accumulation of small quantities of TBP such that it creates a separate organic phase in KCD evaporator EV 3000 (TBP in excess of what can be destroyed) is shown in Figure 6-8. TBP/HPT accumulation from KPA is assumed to have resulted from the transfer of droplets of solvents which are mechanically entrained with the aqueous phase due to improper operation of pulse units. In addition to the diluent wash column (Pulse 3100), two safety barriers were considered for this scenario. The effectiveness of slab settler 3300 to separate out the entrained TBP/HPT is considered as the first barrier. Process sampling in the KCA batch constitution tanks to confirm that the amount of soluble TBP is sufficiently low is considered as the second barrier.

The event tree for a severe process malfunction leading to the transfer of a relatively large volume of solvent is shown in Figure 6-9. There are several different barriers that are designed to prevent such a malfunction. For example, diluent wash KPA-PULSE 3100 is designed and operated such that it potentially could break up any TBP transferred in the form of emulsion. Third phase formation is also controlled by addition of appropriate chemical agents. Similar to the event tree shown in Figure 6-8, there are two safety barriers that can be considered for this scenario. The effectiveness of slab settler 3300 to separate out the separate phase TBP/HPT is considered as the first barrier. Process sampling in the KCA batch constitution tanks to confirm that the amount of soluble TBP is sufficiently low is considered as the second safety barrier. The event tree also includes the paths for the TBP/HPT to be introduced via the KWG drip tray gallery. For this to occur, it is assumed that the TBP/HPT is introduced to the drip trays due to some unknown malfunction such as failure of the slab settler.

6.7.4 Description of the Event Tree Headings

A brief summary of the various headings used in the event trees is provided here. Each individual summary of an event tree heading includes the description of the heading, the definition of success criteria including the major failure paths, and the modeling approach.

Solvent Transfer Mechanical Entrainment

This event tree heading relates to operational malfunction in any of the three KPA pulse units: Pulse 2200, 3000, and 3200, causing an excessive amount of organics to be transported downstream into the KPA diluent wash column 3100. Per empirical evidence, this event is expected to occur with a frequency of about 1 per year. Assuming this is an estimate per pulse column, a frequency of about 3 per year for this top event is assumed in this study. This estimate is constructed on a weak empirical basis therefore it is expected to be uncertain. For the purpose of this analysis, the estimate is assumed to be log normally distributed with an error factor of 3.

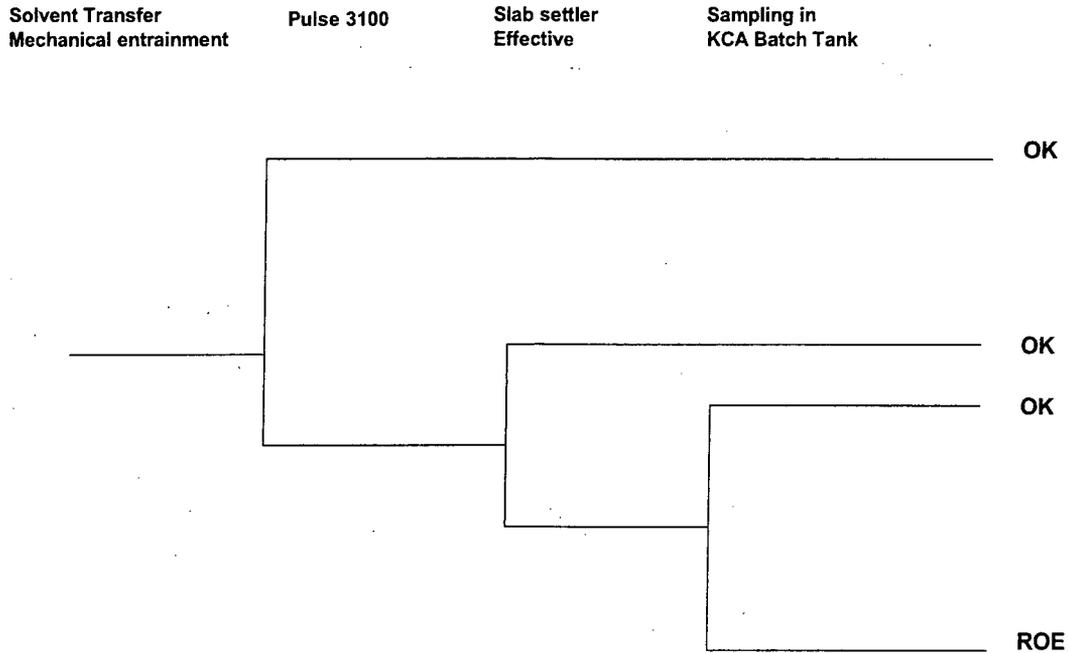


Figure 6-8. Event Tree for ROE in KCD-EV 3000 due to Solvent Transferred by Mechanical Entrainment.

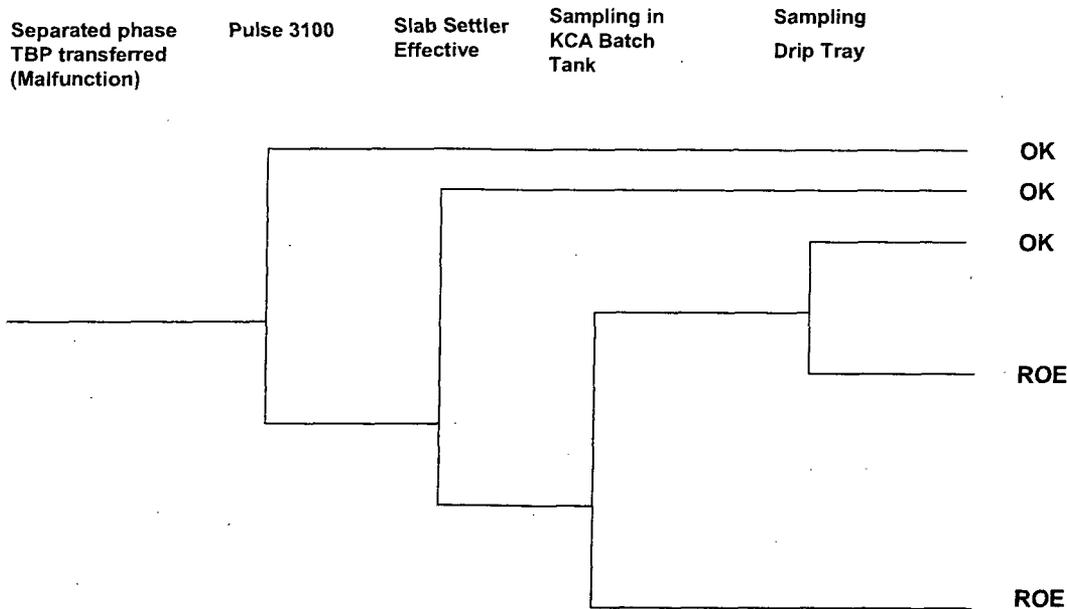


Figure 6-9. Event Tree for ROE in KCD-EV 3000 caused by Transfer of Separated Phase of Solvent due to Severe Process Malfunction.

Pulse 3100

This heading represents the success of the wash column 3100 to break up and separate the entrained organics transported as a result of an operational malfunction. There is currently no empirical data to support a formal estimate of the failure of the wash column to break up and extract the organics. A subjective failure probability with a mean of 0.25 and error factor of 3 is assigned assuming lognormal distribution.

Slab Settler Effectiveness

This heading represents the success of the slab settler to prevent the transfer of organics, in excess of their solubility limit, which could be inadvertently introduced by malfunction of the KPA pulse columns upstream of the KCA batch tanks. The slab settler is a passive feature that utilizes its design to produce a settling time that allows the density differences between the separate phase solvent and the aqueous solution to cause the segregation from one another. A weir in the slab settler prevents the lighter density separate phase solvent from moving downstream to the KCA and KCD units. The slab settler consists of two chambers separated by a baffle. The two chambers in the settler communicate through an opening. A schematic drawing of the settler that displays the overall design and the location of the levels of the organic and aqueous phases is shown in Figure 5-7 in Chapter 5.

The slab settler is made of 304 L stainless steel, has a useful volume of 20 L, and is geometrically safe (a slab) for the plutonium nitrate reference fissile medium. Plutonium

nitrate solution from the plutonium diluent washing pulsed column is fed to the slab settler. The arch drain pipe and the settler chambers are also connected. The arch drain is fed to the CLMN 6000 via an Airlift AL3330. Any organic phase in the solution will separate in the settler, since the organic phase and the aqueous plutonium nitrate solutions are non-miscible. The lighter organic phase will rise to the top of the liquid while the plutonium nitrate aqueous solution remains on the bottom. The solution remains in the slab settler long enough to ensure separation of any organic solvent from the solution. A failure or blocking of the arch drain connection will terminate the flow out of the settler drain; therefore it is not considered a failure for ROE concern. A siphon device is also provided to empty the slab settler to the plutonium rework tank TK8500. The siphon device uses an air ejector to induce a vacuum in the siphon device. The vacuum draws the solution from the slab settler through the siphon device. From the siphon device, the solution drains to the plutonium rework tank.

Density is measured and controlled in the KPA slab settler to ensure that the organic solution (TBP/ HPT) is not transferred downstream to the oxidation column. At a low density threshold of 980 Kg/m^3 , the low density transmitters KPA-DT3300A/B transmit a signal to the low density controllers KPA-DLC3300 A&B which in turn signal KPA-AOV3331 A/B to close. Closing of either one of these redundant IROFS valves stops the air flow to AL3330, which stops transfer of process solution from KPA-SET 3300 to KPA-CLMN 6000. Settler operation is optimized and settling time is controlled by flow into and out of the settler. Over-draining a settler due to operational failures could result in transfer of the organic layers via AL3330 if the active engineered density monitors fail. Operational failures similar to what were described above could still be detected by the density monitors, which are also modeled via fault trees for the slab settler. The only other settler failure mode considered for this study is loss of internal integrity, i.e., failure of the baffle due to corrosion or any other reason. These various failure modes of the slab settler are discussed below.

a. *Slab Settler Operational Failure*

Operational practices for the slab settler are designed to ensure that the density interface on the settling side of the settler does not drop below the weir height. This is done by ensuring that the settler is initially filled with the heavier aqueous material, and by controlling the flow such that sufficient settling time for the separation of organics from aqueous is provided. If such operational failures occur, the active engineered density loop could detect the low density interface below the weir wall and shut the air lift on the drain line, thereby stopping the transfer. Therefore, a failure of the active engineered system is necessary for any operational malfunction to result in a transfer of the organics upstream of the slab settler to the oxidizer column 6000. It should be noted that the density monitor response time is of the order of seconds. The licensee's analysis, assuming a 10 second response time for density monitors and nominal flow rates, showed that the amount of TBP transferred is negligible for ROE concerns.

Two operational malfunctions, when combined with the failure of the active engineered system, are considered as a system failure. These are: failure of administrative control to initially fill the slab settler with heavy aqueous solution and failure to control flow such that insufficient time is available for separation to take place (over-draining). To estimate the potential frequency for such operational mishaps, data for loss of feed water control in NPPs was considered to be a possible surrogate for this failure mechanism. This data shows a probability of about 0.1 per demand. A pilot testing of the slab settler provided

in a supporting document [CETL-4003-EXP-0003, Experimental Final Report Concerning the Efficiency of the Slab Settler to Separate Organic materials from an Aqueous Plutonium Nitrate Solution] reported a failure rate of about 0.05 based on one case out of 21 case runs that the settler did not perform effectively (1/21 = 0.05 per demand).

b. Slab Settler Active Engineered Density Monitors

The active engineered system for the slab settler consist of two density transmitters KPA*DT3300 A/B, two density controllers KPA*DLC3300A/B, and automatic isolation valves KPA*AOV3331 A/B to prevent: (1) the introduction of solvent into equipment which can operate at a temperature above the safety (LFL) limit and (2) the aqueous/organic interface on the settling side of the slab settler (KPA*SET3300) from dropping below the weir. The fault tree models are developed for evaluating the failure probability of this active engineered safety system taking into account the following considerations.

Pneumercators are used for density monitors. They have a precision of about 2% but they require compressed air and periodic precision calibration. Various failure modes of the pneumercators have been observed and could be postulated. These are:

1. Blockage of the dip legs
2. Insufficient or loss of charging air
3. Failure to periodically calibrate properly, and
4. Lack of response or slow response when they are operated for a long time at high or low range.

As is evident from the types of failures identified above, the failure rate for pneumercators is a function of the calibration interval and the service condition. A generic failure rate of $1.13E-5$ per hour for level measuring instruments is currently used for this study and could be modified pending additional information.

c. Failure or Loss of Integrity of the Slab Settler Baffle

The failure or loss of integrity of the baffle area due to erosion and corrosion is also considered as a failure mechanism. The data on corrosion in hot (boiling) nitric acid that is relevant to possible corrosion failures of the baffle indicates that for 65 wt% HNO₃, type 304 stainless has a corrosion rate of 0.2 mm/year [and type 316 stainless of 0.3 mm/year]. The baffle material is SS 304 and it is 5 mm thick. The baffle itself is not under any loading or tensile stresses. Therefore, the mean time between failures estimated based on loss of 1/2 thickness is about 12.5 years which corresponds to failure rate of $(9.0E-6)$ per hour. Given failure of baffles, it is assumed that the organics can be inadvertently transferred if the height of the organic phase falls below the opening of the arched drain tube and the density loops do not shutdown the discharge. For this study, it is assumed, conservatively, that the organic height always falls below the inlet of the arched drain line.

Sampling in KCA Batch Tanks

This heading refers to successful detection of the organics via sampling of the KCA batch tanks, therefore preventing the organic from reaching the high temperature

components in KCD. The batch constitution tanks are annular tanks of 600L each. These are sampled approximately at the rate of 2.2 batches per week and 2 samples per batch, via mixing and three air lifts. This is very similar to the other sampling measurements modeled in Section 6.4 above. The samples are analyzed for many things but are specially monitored for TBP and pH. TBP measurements are done with an HPLC analyzer (2 channels per analyzer) and the pH with a pH measurement device. Similar to other sampling models, it appears the failure rate is driven by human errors associated with drawing off or analyzing samples. In the unlikely event that the solvent passes through the KPA slab settler in such amounts that it could become a separate phase in the KCD evaporator, process sampling in the KCA batch constitution tanks is credited in the PRA to confirm that the amount of soluble TBP is sufficiently low. Thus, these sample points and the associated administrative IROFS are considered to ensure the sample is representative of the contents of the tank (i.e., vessel isolation, vessel homogenization, sample line purging, sample vial traceability, laboratory sampling process, and communication of results from laboratory to the control room).

Sampling in Drip Trays

A drip tray within the process cell in the KWG unit collects leakage from the equipment in the room. Leakage collected in the drip tray is sampled and analyzed before it is transferred to the KCD unit. In the event that the liquid in the drip tray contains solvent, it is not transferred to a KCD unit, but is instead transferred via a remote pump into a drum for proper disposition, since steam jet operations result in elevated temperatures. The objective of this heading is to ensure that a sample is taken to establish the source of the leak and ensure detection of organic prior to using a steam jet and transferring to KCD unit. The typical sampling model is used to construct a fault tree for this case.

The point estimate frequencies of ROE shown in Table 6-11 are due to the sequences displayed in Figure 6-8 and 6-9. These refer, respectively, to ROE due to solvent transfer by mechanical entrainment, ROE-EV3000-STME, and ROE due to separate phase TBP transfer caused by severe process malfunction and subsequent failure of sampling in the batch tank, ROE-EV3000-FBT, or in the drip tray, ROE-EV3000-FDT. The point estimate frequencies range from about 9E-06 per year for solvent transfer by mechanical entrainment, to 3E-06 per year for solvent transfer caused by severe process malfunction, and subsequent failures of sampling in the batch tank, and about 6E-7 per year for sampling failures in the drip tray.

Table 6-11. Frequency of ROE Sequences at EV3000 (per year).

Sequences	ROE-EV3000-STME (IE frequency: 3 per year)	ROE-EV3000-FDT (IE frequency: 1 per year)	ROE-EV3000-FBT (IE frequency: 1 per year)
ROE Frequencies	9.2E-06	5.8E-07	3.1E-06

Table 6-12 provides an uncertainty analysis for the EV 3000 ROE scenarios using the Monte Carlo simulation provided in the SAPHIRE code.

Table 6-12. Summary of Uncertainty Analysis for ROE Sequences of EV3000 Scenarios.

Sequences	Point Estimate Frequency per Year	5 th percentile	95 th percentile	Main Contributors (dominant cutsets)
ROE-EV3000-STME	9.2E-06	6.0E-07	3.4E-05	KCA-FET-SAMP-X-OP-FOP (Fraction of time between successive samplings) KCD-PDW-3100-X-OP-FOP (Failure of diluent wash at pulse 3100) KPA-ALX-3330-X-OP-FOP (Failure of air lift to stop process solution transfer) KPA-OPER-XXXX-X-OP-FOP (Operational failures of slab settler)
ROE-EV3000-FDT	5.8E-07	2.6E-08	2.3E-06	KCD-LAB-ALYS-1-OP-FOP (Failure of analysis of samples at drip tray) KCD-PDW-3100-X-OP-FOP (Failure of diluent wash at pulse 3100) KPA-ALX-3330-X-OP-FOP (Failure of air lift to stop process solution transfer) KPA-OPER-XXXX-X-OP-FOP (Operational failures of slab settler)
ROE-EV3000-FBT	3.1E-06	2.0E-07	1.1E-05	KCA-FET-SAMP-X-OP-FOP (Fraction of time between successive samplings) KCD-PDW-3100-X-OP-FOP (Failure of diluent wash at pulse 3100) KPA-ALX-3330-X-OP-FOP (Failure of air lift to stop process solution transfer) KPA-OPER-XXXX-X-OP-FOP (Operational failures of slab settler)

The point estimate frequency of ROE occurrence at EV3000 due to solvent transfer by mechanical entrainment is about 9.2E-06 per year. The dominant cutsets contributing to this frequency are: failures of sampling between successive sampling intervals in the KCA batch tanks to detect organics in case of the solvent transfer by mechanical entrainment, failure of diluents wash at Pulse 3100, the failure of the single air lift to stop the transfer of process solution from KPA-SET 3300 to KPA-CLMN6000, and operational failures of the slab settler.

In case of a severe process malfunction leading to the transfer of a relatively large volume of solvent, if the slab settler fails to stop the transfer of the solvent, the failure of detecting organics via either the sampling at KCA batch tank (indicated by sequence

ROE-EV3000-FBT in Table 6-12) or the failure of sampling at the drip tray (indicated by sequence ROE-EV3000-FDT in Table 6-12) will cause an ROE excursion. The annual frequencies of the ROEs are $3.1E-06$ and $5.8E-07$ per year, respectively.

For the sequence ROE-EV3000-FBT, the dominant contributions come from the failures of diluents wash at Pulse 3100, the failure of the single air lift to stop the transfer of process solution from KPA-SET3300 to KPA-CLMN6000, and operational failures of the slab settler during one sampling interval of the KCA batch tanks. To model the fault exposure time caused by the sampling interval of KCA batch tanks, a basic event is introduced to facilitate the probability calculations. This basic event is described in Table 6-10 as "Fraction of time between successive samplings," and it is denoted as "KCA-FET-SAMP-X-OP-FOP."

For sequence ROE-EV3000-FDT, the dominant contributions come from failures of sample analyses at the KCD drip tray to detect organics, the failure of diluents wash at Pulse 3100, the failure of the single air lift to stop the transfer of process solution from KPA-SET3300 to KPA-CLMN6000, and operational failures of the slab settler.

References

- 6-1. Shaw Areva MOX Services, "Chemical and Radiolytic Heat Generation in Pre-Autocatalytic Tributyl Phosphate Solutions," DCS01 RRJ DS CAL H 35362.
- 6-2. V. Mubayi, M.A. Azarm, W. Mukaddam, and R.A. Bari, "Risk Assessment of Red Oil Excursions in the MOX Facility," Brookhaven National Laboratory, BNL-MOX-2007-001, March 2007.

DRAFT

7. SUMMARY AND CONCLUSIONS

The study presented in this report is an analysis of issues related to the risk of red oil excursions (ROE) in the proposed MOX Facility (MFFF) and contains insights that could be useful in staff reviews of the MFFF License Application. The objective of the study is to provide an independent assessment of the risk of ROE in the MFFF based on the design contained in the license application (LA) [7-1] submitted by the applicant for an operating license and analyzed by the licensee in the accompanying Integrated Safety Analysis Summary (ISAS) [7-2]. This effort is a part of a larger program of technical assistance to NRC staff in the area of risk-informed decision making for fuel cycle facilities. It is clearly understood that the results of the study are meant to convey an independent perspective on risk to the NRC staff. They are not meant to serve as the basis for any determinations related to facility licensing that will be made under the requirements of 10 CFR 70.

BNL carried out an earlier study of the risk significance of the red oil phenomenon based on the design of the MFFF revealed in the CAR [7-3]. That study was limited because the CAR design was preliminary, particularly with respect to the safety strategies utilized for prevention and mitigation of red oil events in various process units. However, the study did identify and rank the risk significant systems and operations in the MFFF for red oil excursions based on the CAR system design and provided risk insights to NRC staff to assist in a more risk-informed review of the design proposed by the applicant.

7.1 Red Oil Phenomenon

The MFFF uses a solvent extraction process, similar to that used in fuel reprocessing plants, to remove impurities from the feed consisting of weapons-grade plutonium. The extraction operation employs the solvent tributyl phosphate (TBP), diluted in hydrogen propylene tetramer (HPT), as an extractant along with concentrated nitric acid in various processes. The ROE phenomenon generally refers to the explosive, runaway nitration-oxidation reaction that can occur when the organic solvent TBP, and its degradation products, comes in contact with concentrated nitric acid at elevated temperatures. Such events have occurred before, in the U.S. and other countries, in facilities that employ extraction technology similar to what is proposed to be used at the MFFF. These reactions occur continuously over a wide temperature range but the reaction rates and the heat and gases generated at lower temperatures below about 60 °C are low and passive heat removal and normal venting are adequate. At higher temperatures (about 80°C and higher), facility-specific heat removal measures are needed along with actions to ensure that the amount of TBP that can enter heated acid-bearing vessels is limited.

The phenomenology and chemistry of ROEs is reviewed in Chapter 3, along with a discussion of various factors that can promote the occurrence of a ROE. The red oil reaction analyzed in this report is focused on TBP-nitrate thermal reactions. It is possible that radiolytic dissociation of organic compounds could lead to the formation of more reactive species that could promote ROEs. However, the quantities of radionuclides involved in the MFFF are fairly small compared to those in fuel reprocessing plants and their decay rates are also low; this radiolytic dissociation was not considered in the study.

7.2 Safety Strategies for Red Oil at MFFF

The safety strategy and approach for coping with the possibility of ROEs proposed in the LA and analyzed in the ISAS is significantly different from what was discussed and assessed in the CAR design. The overall strategy consists of three elements:

1. Segregation of separate phase solvent (TBP) from acid bearing and heated process equipment such as evaporators; this is meant to ensure that a separate phase of TBP or TBP in excess of its solubility limit that could be entrained with the aqueous phase does not come into prolonged contact with highly concentrated nitric acid at elevated temperature. This strategy is implemented through process sampling and density monitoring and control, and also includes a passive engineered system, a slab settler, to allow for the separation of organic and aqueous phases based on their density difference. The IROFS credited for this strategy include sampling points and procedures, process density control loops and monitors, and a slab settler.
2. Heat transfer strategy; this relies on passive convective and radiative heat transfer mechanisms to the surrounding environment. The strategy demonstrates adequate heat transfer to the room environment of heat that may be generated from all possible sources including the exothermic reactions such as the solvent-nitric acid reaction (at relatively low temperatures). The temperature of the surrounding environment is controlled to ensure adequate heat transfer during routine and pre-defined upset conditions. The IROFS credited include: the geometry of process vessels, temperature sensors and control loops to detect and limit self-heating, off-gas venting to relieve pressure from any gases evolved in the reactions, and reagent sampling controls to ensure proper diluent is used.
3. Evaporative cooling strategy; this provides for heat removal via evaporation of water in the aqueous phase in heated process vessels where some (limited) amount of TBP is expected to be present, and where the possibility of the exothermic nitration/oxidation reaction exists. This strategy depends on the large latent heat of vaporization associated with the aqueous phase, and it also requires the fulfillment of certain criteria, such as maintaining a minimum aqueous to TBP ratio, a maximum TBP layer depth, a maximum process solution temperature and an open, vented system. The IROFS credited for this strategy are process sampling and administrative flushing to limit the amount of TBP accumulation, level controls to maintain the minimum aqueous to TBP mass ratio, temperature controls to limit solution temperatures, and an offgas venting system to relieve pressure from gases released in the reactions.

7.3 Limitations of the BNL Study

The BNL study is a limited-scope probabilistic risk assessment (PRA) model that evaluated the failure of some of the safety strategies due to internally initiated process deviations. In particular, the PRA model focused on (1) the failure of evaporative cooling in selected process vessels, and (2) the failure of the TBP prevention strategy, through such events as emulsification, and the formation of a third phase or a rag layer, leading, eventually, to a violation of the success criteria for evaporative cooling. The PRA can be considered a limited-scope risk assessment for several reasons:

1. The generic risks due to external hazards, such as seismic events, internal fires, or loss of offsite power events, including station blackout, were excluded from the analysis. These initiating events can potentially lead to other high consequence outcomes, similar to ROEs, and would have greatly enlarged the scope of the study, which is limited to ROEs only. Also, according to the ISA Summary, the applicant has taken a number of steps and actions through the installation of IROFS to reduce the likelihood of internal fires as well as the likelihood of externally initiated event sequences to low values consistent with the highly unlikely category of event frequencies.
2. Second, the red oil reaction analyzed in the study accepted broadly the characterization of the red oil phenomenon developed by the applicant by focusing on thermal decomposition reactions alone. The impact of radiolytic dissociation on the red oil reaction was not considered because radiolysis would have a relatively minor impact in the MFFF as the concentrations and decay rates of the radionuclides involved are relatively low.
3. Failures of the heat transfer strategy were not considered in the analysis. This strategy applies to the adequacy of passive heat transfer to the room environment from process vessels containing solutions at lower temperatures (about 55 C and below) and depends for its success on the availability of room cooling, i.e., the proper operation of the facility's HVAC system. Consideration of the failures of the HVAC system, however, would have greatly enlarged the scope of the analysis, which is limited to ROE.
4. The semi-empirical model for the TBP-nitrate reactions developed by the applicant, mentioned in Chapters 3 and 6 above, and used to set the success criteria for the evaporative cooling safety strategy, was accepted as the basis for further evaluation of the phenomenon. The applicant considers this model to be conservative as it is based on the heat generated in a pure TBP-nitric acid reaction rather than 30%TBP-70% HPT mixture that will be used at MFFF. However, its results are based on the selection of one particular set of experiments as broadly representative of the heat evolved in TBP-nitrate reactions. Any independent assessment of the limitations of this model, however, was considered far beyond the scope of the PRA.

7.4 Qualitative Assessment of ROE

Chapter 5 of the report provides a qualitative assessment of the factors that may contribute to the possibility of ROE in the various process units comprising the Aqueous Polishing (AP) Unit. There are eight process units within the AP process where organics and nitric acid either contact each other during normal operation or have the potential to come into contact. These are: (1) Purification cycle (KPA), (2) Solvent recovery (KPB), (3) Oxalic precipitation and oxidation (KCA), (4) Oxalic mother liquor recovery (KCD), (5) Acid recovery (KPC), (6) Aqueous waste reception (KWD), (7) Solvent waste reception (KWS), and (8) Laboratory liquid waste receipt (LGF). These eight units are potential candidates where ROEs can occur; the BNL study focused on units (1) through (5) since the process conditions there place them at a somewhat higher risk of a ROE compared to units (6) through (8). Each of the five process units was evaluated for the

possibility of a ROE in terms of the equipment employed, the sequence of operations, and the conditions (temperature, pressure, etc.) under which the operations occur.

Based on the heat sources present, the heat balance and the potential for TBP transfer, four vessels in two process units were selected for more detailed evaluation. These were the first and second stage evaporators EV 2000 and EV 6000 in the acid recovery unit, the concentrates collection tank TK 3000 in the acid recovery unit, and the evaporator EV 3000 in the oxalic mother liquor recovery unit.

For each of the vessels selected, a qualitative safety review was performed followed by a quantitative risk assessment of ROE. The qualitative review is summarized first followed by the quantitative risk assessment in the next section.

EV 2000 is a natural recirculation thermosiphon type boiler, which utilizes pressurized super heated water as a heating fluid. Nitric acid vapor distillates from this evaporator are condensed and routed to a feed buffer pot that decouples operation of the first evaporator from the second evaporator. EV2000 operates under vacuum. The normal process temperature is below 66°C and the normal super heated hot water temperature is 105°C (221°F). The hot water system temperature is equipped with controls to ensure a maximum temperature of 122°C (251.6°F) is not violated. The red oil prevention strategy applied to EV 2000 is evaporative cooling. Two conditions are necessary for a viable ROE scenario to occur: (1) a rising process temperature above 80°C (176°F); this can be due to an inability to maintain the hot water system temperature below 122°C (251.6°F) or the occurrence of a heat exchanger tube rupture, and (2) failure of evaporative cooling to successfully mitigate the event and prevent the occurrence of ROE. The success criteria for evaporative cooling involve maintenance of a minimum aqueous phase to TBP ratio, a maximum TBP layer depth, a maximum process solution temperature, and an open adequately vented system. Chapter 6 provides an analysis of the conditions under which these criteria could be violated. These include equipment failures (loss of temperature control, heat exchanger tube ruptures, venting system failure), human failures (operator failure to flush the system on schedule as required), and process failures (formation of emulsions, or a third phase or rag layer).

TK 3000 is a collection tank for concentrates drawn off from EV 2000 and contains a high level of alpha emitting impurities, mainly americium, for transfer to the high alpha liquid waste area of the KWD unit. The tank is cooled by a cooling water loop, and is maintained in a well-mixed condition by an air sparger to prevent the formation of any hot spots within the tank that could lead to an initiation of a ROE. TK 3000 operates normally at a temperature around 40°C. If the temperature reaches a set point of 80°C (176°F), steam jets will be shut off, and the solution volume is verified and maintained at 42 liters to ensure that the evaporative cooling would be successful. The red oil safety strategy for the concentrates collection tank TK 3000 is also evaporative cooling. A six-monthly flushing of the tank contents is performed to ensure that any accumulation of TBP is limited to an amount that is within the criteria for successful evaporative cooling. Semi-annual flushing ensures that the amount of TBP is limited to 21 liters in the tank. Two conditions are necessary for a viable ROE scenario to occur: (1) a rising tank temperature to 80°C (176°F) due to failure or degradation of the tank cooling/mixing system and (2) failure of evaporative cooling. Chapter 6 provides an assessment of the conditions under which the success criteria for evaporative cooling in TK 3000 could be violated.

EV 6000 is a natural recirculation thermo-siphon type boiler that utilizes pressurized steam at approximately 2 bar gage and 133°C (271.4°F) as a heating fluid. Distillate from EV 2000 is re-evaporated in steam heated EV 6000. The conditions for a ROE in EV 6000 exist if sufficient TBP is present. Hence, the red oil safety strategy for evaporator EV 6000 is TBP prevention, viz. the sampling instrumentation and density monitors installed to prevent an excessive amount of TBP transfer from the KPA to the KPC unit. While process upsets in EV 2000 could conceivably transfer TBP to EV 6000 via entrainment, further analysis showed that any separate phase transfer was unlikely and easily detectable since it would cause a loss of the vacuum seal between EV 2000 and EV 6000, which would lead to a shutdown of the KPC unit. The small amount of soluble TBP transferred would be easily destroyed in the conditions prevailing in EV 6000. Hence, as discussed in detail in Chapters 5 and 6, the possibility of TBP accumulation in EV 6000 is significantly lower than in EV 2000 so the scenario for ROE in EV 6000 was not modeled quantitatively but was screened out qualitatively.

EV 3000 is a natural circulation thermo-siphon evaporator which concentrates the oxalic mother liquors, supplied from a feeding tank TK 2000. The evaporator includes a boiler used for evaporation of the feed solution and reflux from the rectification column. It has a tubular heat exchanger. The heating fluid (steam) occupies the shell side and the mother liquor to be evaporated circulates in the tubes. The conditions for a ROE in EV 3000 readily exist only if sufficient TBP is present. Hence, TBP prevention is the main red oil safety strategy applied to this evaporator. The amount of TBP that enters the evaporator from the feeding tank TK 2000 is controlled below its solution detection limit of 50 mg/liter. This small amount of TBP will be fully and safely reacted in the aggressive environment that exists in this evaporator. This study conservatively assumes that the ROE could occur if the soluble TBP amount is not controlled or if a separated phase of TBP is transferred to the evaporator. Ways in which TBP transfers above the solution limit could occur are discussed in Chapter 6. These could happen either through a slow accumulation of mechanically entrained droplets that eventually create a separate phase of TBP or a severe process malfunction leading to a transfer of a relatively large amount of solvent from the KPA unit. Both ways of TBP transfer involve the circumvention of multiple barriers, including the diluent wash pulse columns in the KPA unit, the passive slab settler at the back end of the KPA unit and the process sampling controls in the KCA batch constitution tanks that ensure that the amount of soluble TBP passing through the unit downstream to the KCD evaporator remains sufficiently low. Operational failures in the pulse columns, the slab settler, and the sampling controls that could allow TBP transfer to EV 3000 are analyzed in Chapter 6.

7.5 Quantitative Assessment of ROE

Quantitative evaluation, using accident sequence delineation presented in the form of event trees and fault trees, was carried out to gain further insights into possible combinations of failures that could lead to ROE in the process vessels selected after the qualitative assessment, i.e., EV 2000, TK 3000, and EV 3000. The details of the assumptions and models underlying the quantitative assessments are outlined and discussed in Chapter 6 and the fault and event trees are provided in Appendix A. Quantification was carried out using the SAPHIRE code to obtain the point frequency of a ROE and a 5th percentile and 95th percentile frequency to show the range of uncertainty. The results are displayed in Chapter 6.

The ROE scenario in EV 2000 is modeled under two conditions of TBP accumulation: (1) normal accumulation of TBP, which refers to an accumulation of a small amount by mechanical entrainment with the aqueous phase, and (2) upset accumulation of TBP, which can occur due to a severe process malfunction such as formation of an emulsion that can transfer large quantities of solvent.

Under the first condition, high solution temperature and failure of the evaporative cooling strategy is necessary for a ROE to occur in EV 2000. The initiating event for this scenario is the increase in solution temperature which can lead to a ROE if the evaporative cooling strategy fails. This initiating event can happen due to a loss of temperature control or a heat exchanger tube rupture. The former is modeled via a standard fault tree model and the latter via generic data. The next top event in the event tree models the different by which the various success criteria for evaporative cooling, viz., maintaining the aqueous to TBP mass ratio and the TBP layer thickness, can be violated. The first can happen due to operator failure to flush the vessel at the end of a six month period, which is conservatively assumed to cause an unavailability of evaporative cooling for six months until the next flushing action is required. This failure is modeled via a fault tree based on human error probability to carry out an action. The failure probability for the second criterion, maintaining TBP level, is estimated through standard fault tree methodology. The last top event in the tree represents the success of venting to ensure that the solution temperature is maintained below the azeotropic limit for the nitric acid/water solution. Venting is provided by a two-train system consisting of fans and HEPA filters with an additional fan as standby. Failure of venting is modeled via a fault tree to evaluate the venting failure probability. There are two ROE sequences for this scenario; in the first the level control is successful but venting fails, while in the second, the amount of TBP accumulated is sufficient to violate the criteria for evaporative cooling. The dominant cutset in the first sequence is common cause failure of plugging of two sets of HEPA filters. In the second sequence, the dominant cutset is the failure of the operator to carry out the six-month flush out of the vessel.

Under the second condition, multiple failures of the barriers that prevent TBP transfer from the KPA unit to the KPC unit have to occur. The transfer is assumed to begin with a severe process malfunction such as formation of an emulsion in the initial pulse extraction column in the KPA unit. Following this, the diluent washing pulse columns that extract the TBP can also fail in breaking up any organics entrained in the aqueous phase or in inducing a manual termination of TBP transfer. The failure probabilities for these were assigned based on very limited data. Further barriers to the transfer of organics to EV 2000 are provided by sampling controls that detect TBP and density controls that detect HPT. Failure of these controls was modeled via standard fault tree modeling. The initiating event for this scenario is again a loss of temperature control or a heat exchanger tube rupture that leads to a rise in solution temperature. The top events in the event trees relate to the success/failure of the various pulse columns in breaking up entrained organic material followed by the success/failure of the sampling and density controls. Venting is not modeled as the amount of TBP assumed to be transferred in the upset accumulation condition would violate the criteria for the success of evaporative cooling. The dominant cutsets in one sequence are the ineffectiveness of density controls, common cause failure of the density transmitter, failure of sampling analysis, failure of diluent wash column, and malfunction of the pulse extraction column. In the other sequence, the dominant cutsets are ineffectiveness of density controls, fraction of the time sampling failed between successive sampling intervals, failure of diluent wash column, and malfunction of the pulse extraction column.

The PRA model for ROE in tank TK 3000 assumes: (1) failure to provide cooling flow to the tank heat exchanger could result in tank heat up and initiation of evaporative cooling (HVAC system failures that could also lead to tank heat up were not modeled as it was assumed that facility response to HVAC failure would be shutdown of the KPC unit), (2) failure of spray mixing inside the tank could create hot spots leading eventually to initiation of evaporative cooling, and (3) if there was an increased amount of TBP in the tank due to inadvertent transfer, then loss of cooling or mixing would lead to ROE as the criteria for evaporative cooling would have been violated. The initiating event is the loss of cooling or mixing; its frequency was estimated from fault tree evaluations of the systems involved. The next top event is "no transfer of separate organics", which was estimated using the models developed earlier for EV 2000, due to the common pathways for transport of separate phase TBP to the process vessels in the KPC unit, including EV 2000 and TK 3000. The next top event labeled "level control or No excessive TBP" addresses the operator actions needed to provide aqueous make up to maintain the criteria for success of evaporative cooling on the appropriate branches under conditions (1) and (2) above. The last top event in the tree, "venting", represents the success of venting to maintain the solution temperature at a safe level to prevent a ROE. There are four ROE sequences. Two of them involve the transfer of large amounts of TBP to TK 300 due to malfunctions in the pulsed extraction columns and subsequent failures of the sampling and density controls; they are very similar to the scenarios under upset accumulation in EV 2000 and the dominant cutsets are also similar. The dominant cutset in the venting failure sequence is common cause failure of plugging of HEPA filters. In the remaining sequence it is the failure of the operator to recognize the level alarm and take proper action.

The PRA model for ROE in EV 3000 is based on the evaluation of the various pathways by which organics can be transferred to EV 3000. Two scenarios with their respective event trees are modeled; in the first scenario, the initiating event is solvent transfer by mechanical entrainment, in the second by a severe process malfunction leading to the transfer of a relatively large amount of solvent. Both event trees consider the following top events in sequence: pulse 3100; i.e., success of the wash column to break up and separate the entrained organics, slab settler effectiveness in preventing transfer of any separate phase organics in excess of their solubility limit, and sampling for organics in the KCA batch tanks. The second scenario has another top event, sampling in drip trays, that analyzes leakage samples for organic content before transfer to the KCD unit. Slab settler failures involve failures of density controls, which were modeled by fault trees, operational failures that were taken from a supporting document on settler operation, density monitor failures, analyzed by fault trees, and loss of settler baffle integrity, estimated based on corrosion rate data. The other top events, with the exception of the failure of pulse 3100 column, were also modeled by fault tree methods. The details are provided in Chapter 6. Three ROE sequences result from the analysis. The dominant cutsets in all of them include operational failures of the slab settler, failure of diluent wash column pulse 3100 and failure of the air lift to stop process solution transfer to the KCD unit.

7.6 Conclusion

The red oil phenomenon is complex; the reaction takes place over a range of temperatures and the exothermic reaction rate is affected by several factors as analyzed

Official Use Only

APPENDIX A
FAILURE RATE DATA
FAULT TREES AND EVENT TREES

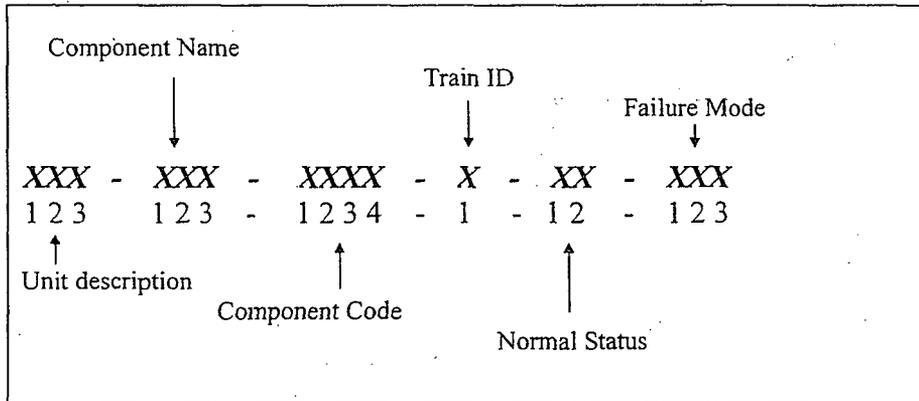
Official Use Only

Failure Data in ROE

Components	Failure Modes	Failure rate per hour or failure probability per demand	Error Factor	Sources
Lab analysis	Error	3.0E-04 per demand	10	SRS
Admin control	Failure	5.0E-03 per demand	10	SRS
Agitators	Failure	6.2E-06 per hour	1.72	WIN330
Jets	All Failures	1.63E-06	1.51	WIN330
Heat Exchanger	Rupture	5.0E-07 per hour	30	
Temperature Element	Failure	1.0E-06 per hour	10	INEL-95/0422
Temperature Transmitter	Failure	3.0E-06 per hour	10	INEL-95/0422
Press Element	Failure	1.0E-06 per hour	10	INEL-95/0422
Press Transmitter	Failure	3.0E-06 per hour	10	INEL-95/0422
Flow Element	Failure	1.0E-06 per hour	10	INEL-95/0422
Flow Transmitter	Failure	3.0E-06 per hour	10	INEL-95/0422
Level Element	Failure	1.0E-06 per hour	10	INEL-95/0422
Level Transmitter	Failure	3.0E-06 per hour	10	INEL-95/0422
HVAC Filter	Failure	1.0E-05 per hour	10	INEL-95/0422
PLCs	Failure	1.49E-06 per hour	10	INEL-95/0422
Indicators	Failure	1.0E-05 per hour	10	INEL-95/0422
Alarm/Annunciation	Failure	3.0E-05 per hour	10	INEL-95/0422
Air lifts	Failure	1.17E-06 per hour	6.63	INEL-95/0422
Density Loops	Failure	1.13E-05 per hour	4.09	INEL-95/0422
Fans	Fail to run	1.0E-05 per hour	10	SPAR Model
	Fail to start	3.0E-03 per demand	10	
Instrumentation Air	Total loss of Instrumentation Air	1.0E-02 per year	(Gamma distribution with $r=0.5$)	SPAR Model
Cooling water	Total loss of cooling water	4.0E-04 per year	(Gamma distribution with $r=0.5$)	SPAR Model
AOVs	Fail to open/close	1.2E-03 per demand	4.3 (Beta distribution with $b=832$)	SPAR Model
AOVs	Fail to control	3.0E-06 per hour	18.8 (Gamma distribution with $r=0.3$)	SPAR Model
Human Cognition	Error	1.0E-02 per demand	5	NUREG/CR-6883
Human Execution	Error	1.0E-03 per demand	5	NUREG/CR-6883
Analyzer	Failure	3.49E-03 per hour	3	PRAM Database

Naming Scheme of Basic Events

Proposed naming scheme for basic events in fault tree model is shown here.



- a). Unit description (XXX) :
 - KPA : Purification unit
 - KPC : Acid recovery unit
- b). Component name (XXX):
 - AOV : Air-operated valve
 - HMN : Human performance related
 - PLC : Programmable logic controller
 - FIX : Flow indicator
 - ALX : Air lift
 - DLC : Density controller
 - DTX : Density transmitter
 - FLW : Low air flow detector
 - PDW : Diluent wash
 - PUL : Pulse column
 - CWS : Cooling water system
 - EXX : Venting
 - HEP : Filter of venting system
 - LLC : Level controller
 - TEX : Temperature transmitter
 - TTX: Temperature sensor
 - THC : Temperature controller
- c). Component ID (XXXX): such as 2003
- d). Train ID (X):
 - A : train A
 - B : train B
 - X : Not applicable
- e). Normal status (XX):
 - NO: Normally Open
 - OP: Operational Mode
- f). Failure Mode (XXX):
 - FTC: fail to close (Normally open)
 - FOP: Fails Operation (non specific)
 - CCF: Common cause failure

Official Use Only

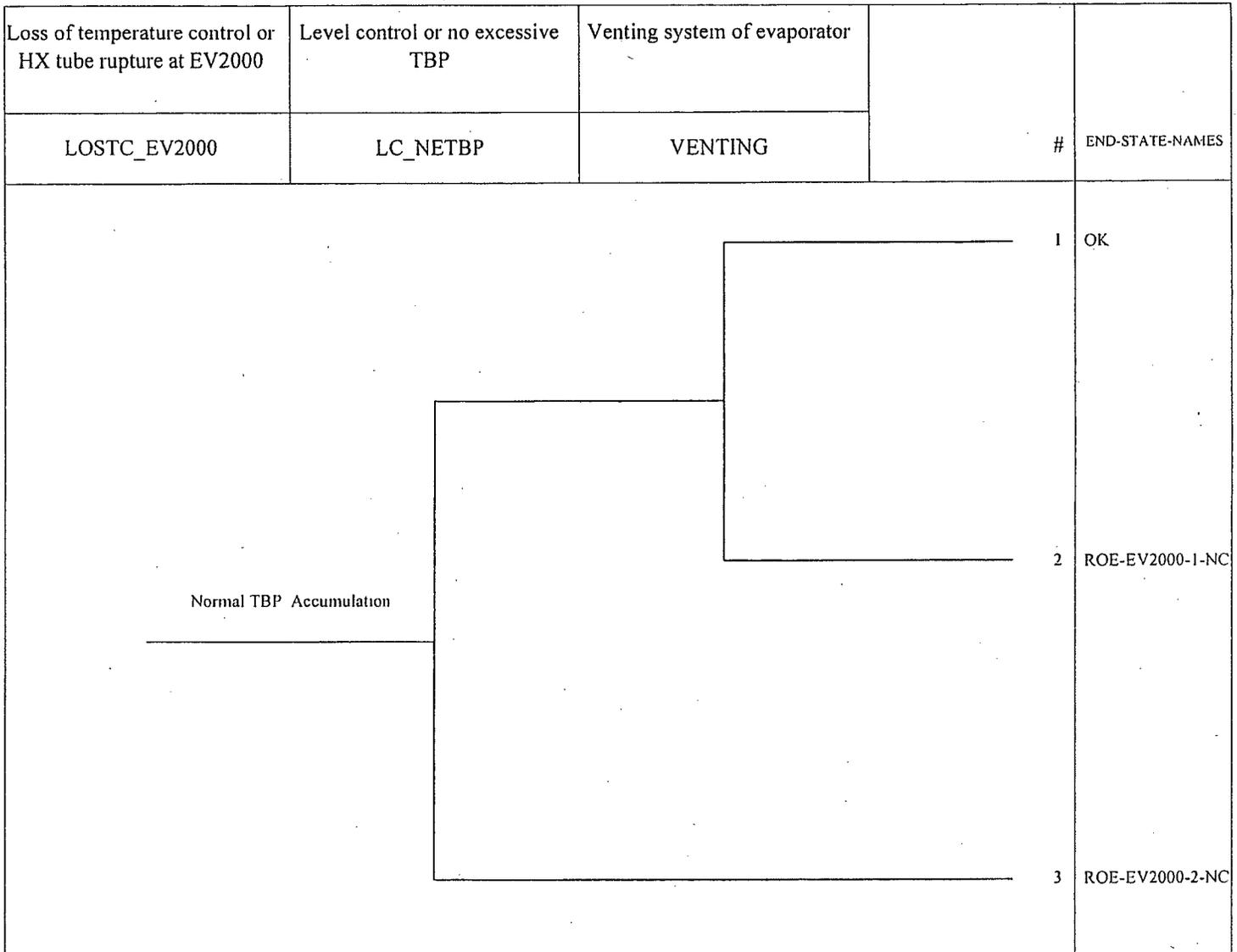


Figure A-1: Event Tree for ROE Scenario at EV2000 under Normal TBP Accumulation Condition

Official Use Only

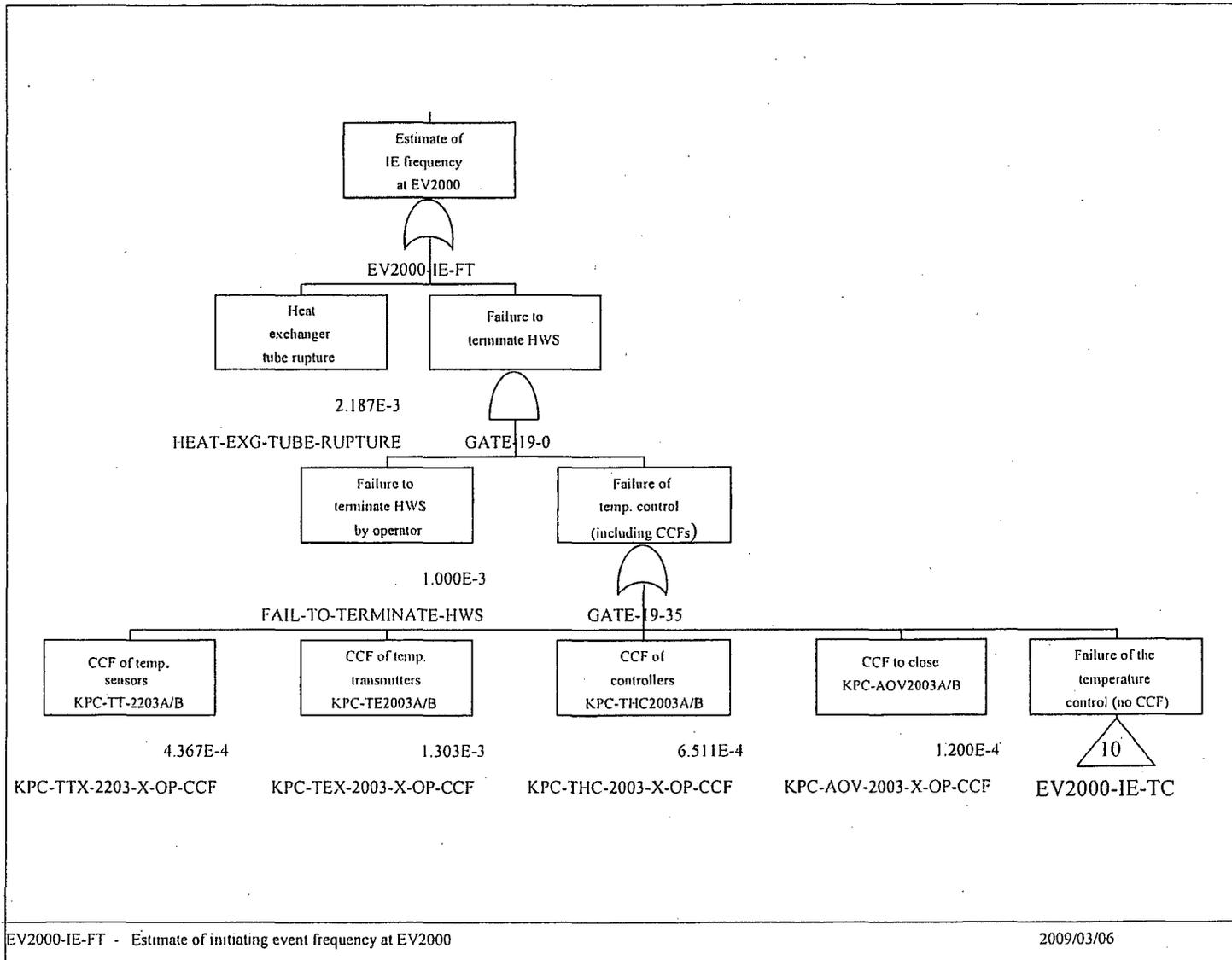


Figure A- 2: Fault Tree for Initiating Event Frequency at EV2000

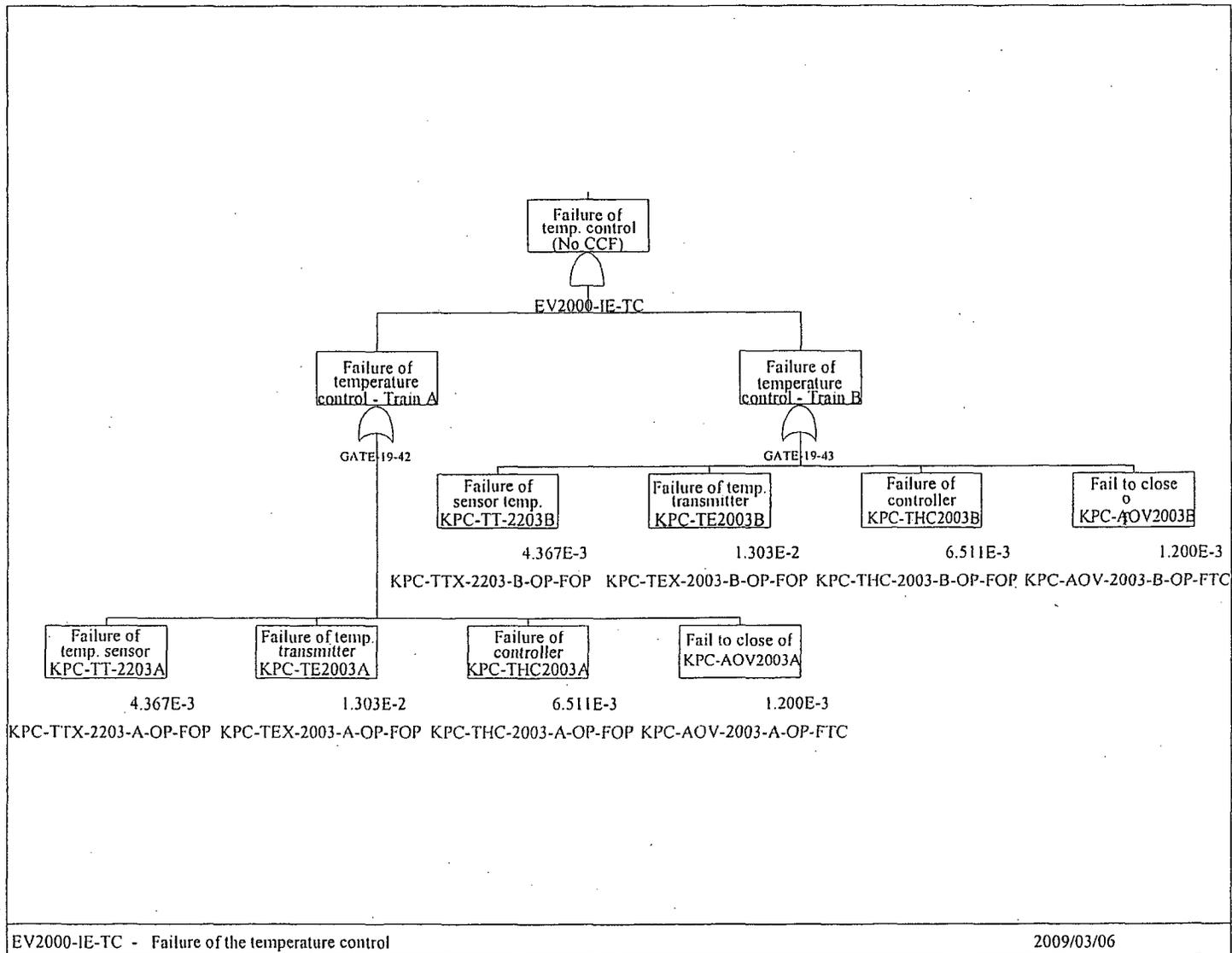


Figure A-3: Failure of Two-train Temperature Control at EV2000

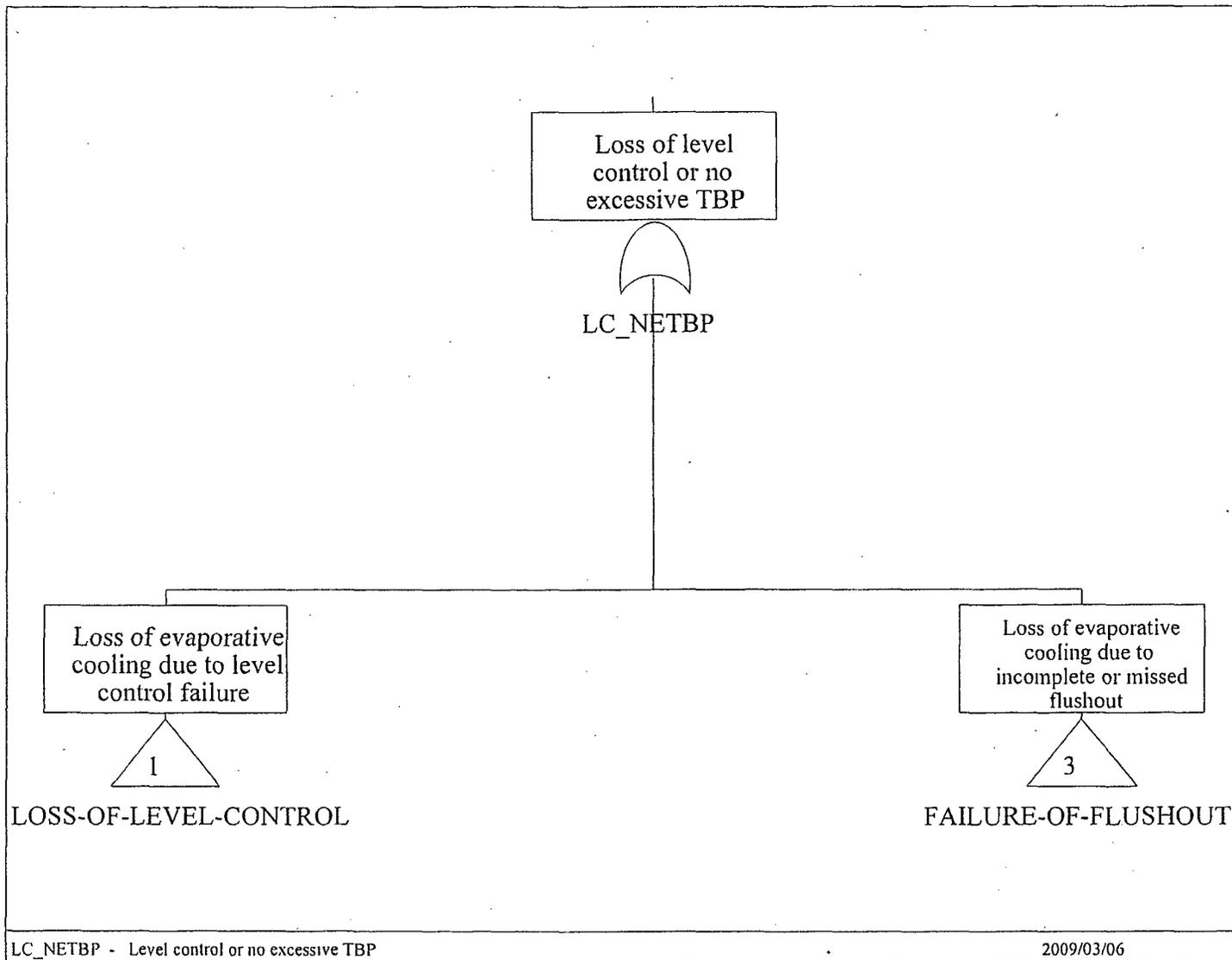


Figure A- 4: Fault Tree for Loss of Level Control or No Excessive TBP at EV2000

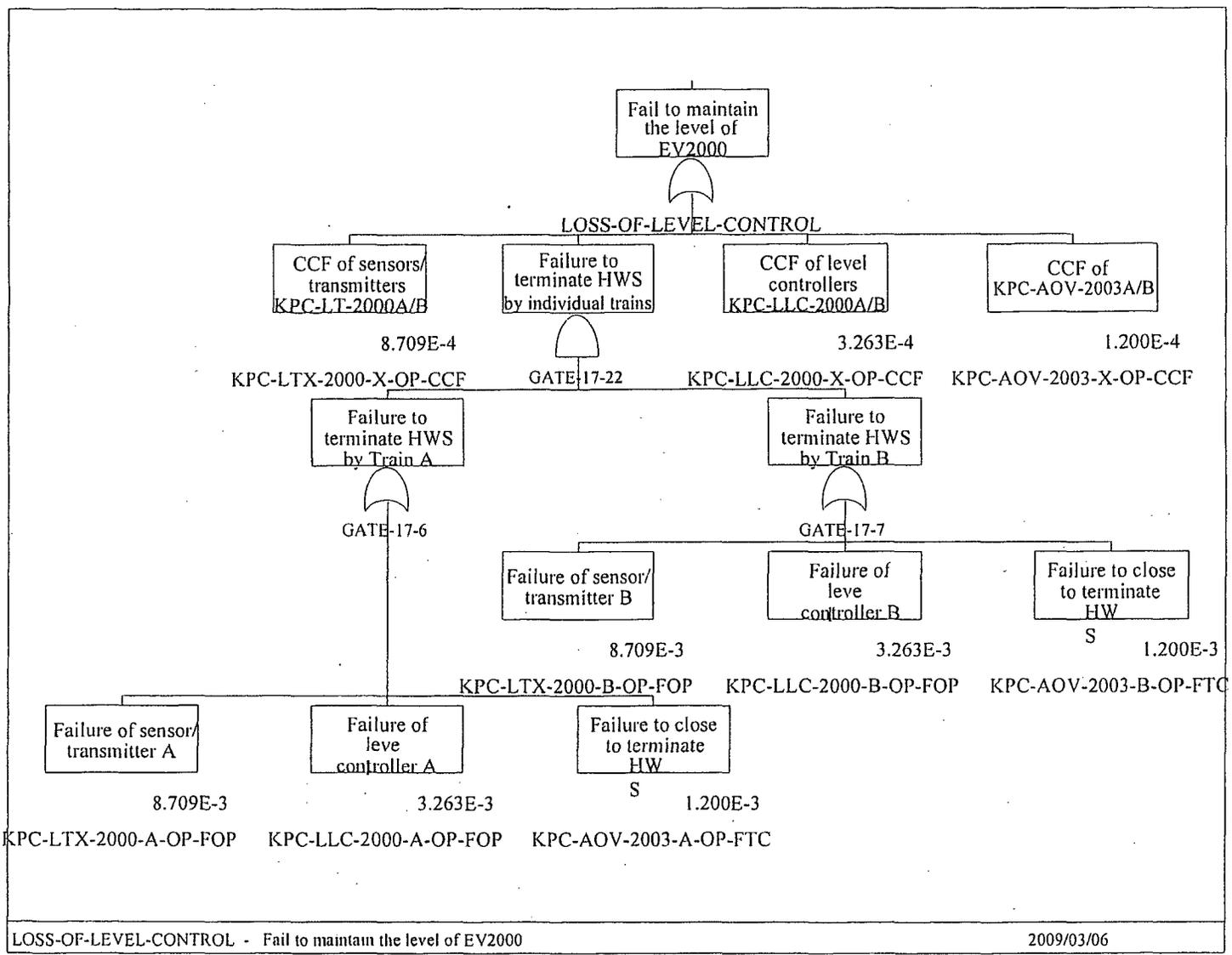
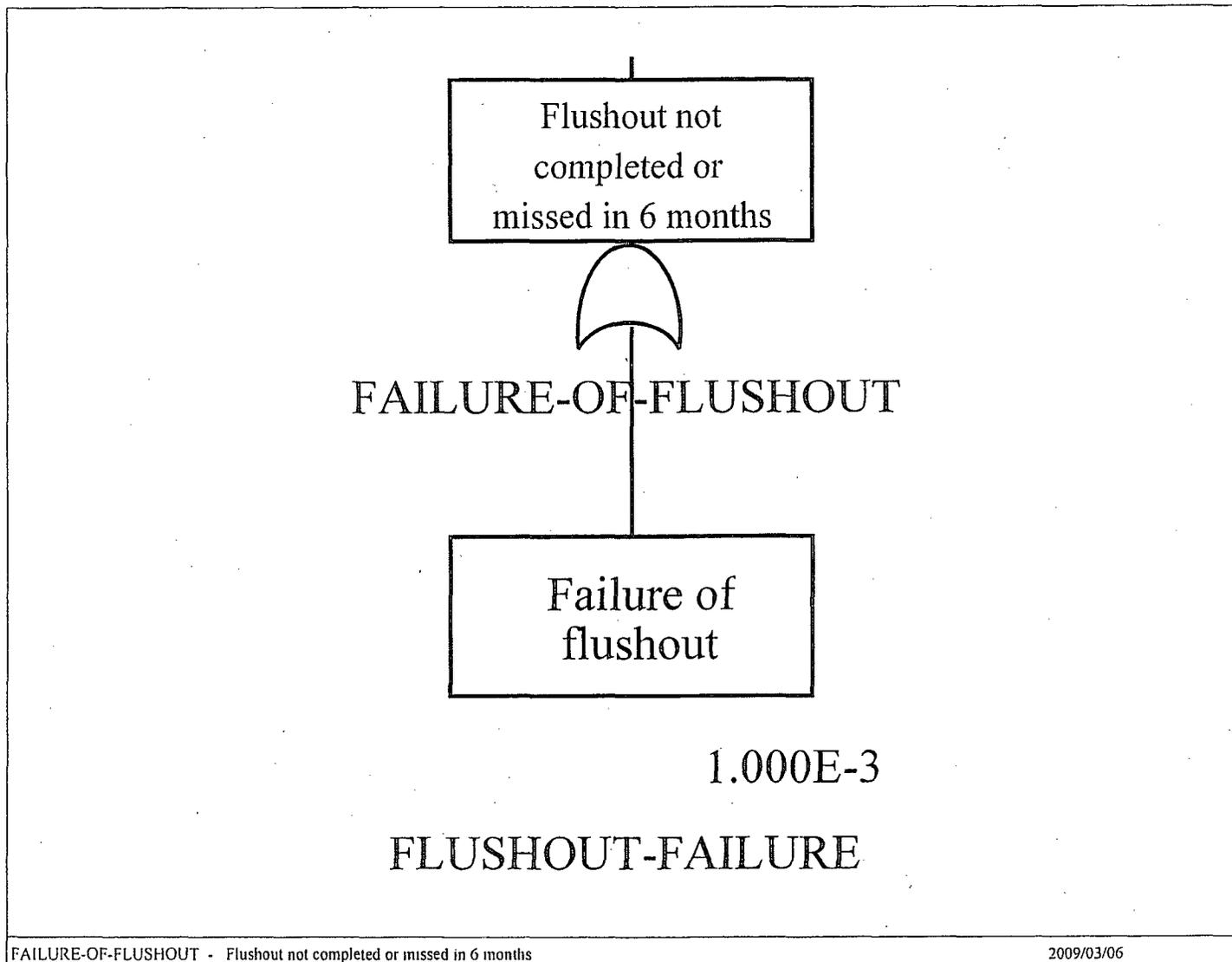


Figure A- 5: Fault Tree for Loss of Level Control at EV2000

Official Use Only



FAILURE-OF-FLUSHOUT - Flushout not completed or missed in 6 months

2009/03/06

Figure A- 6: Failure to Flush Out EV2000

Official Use Only

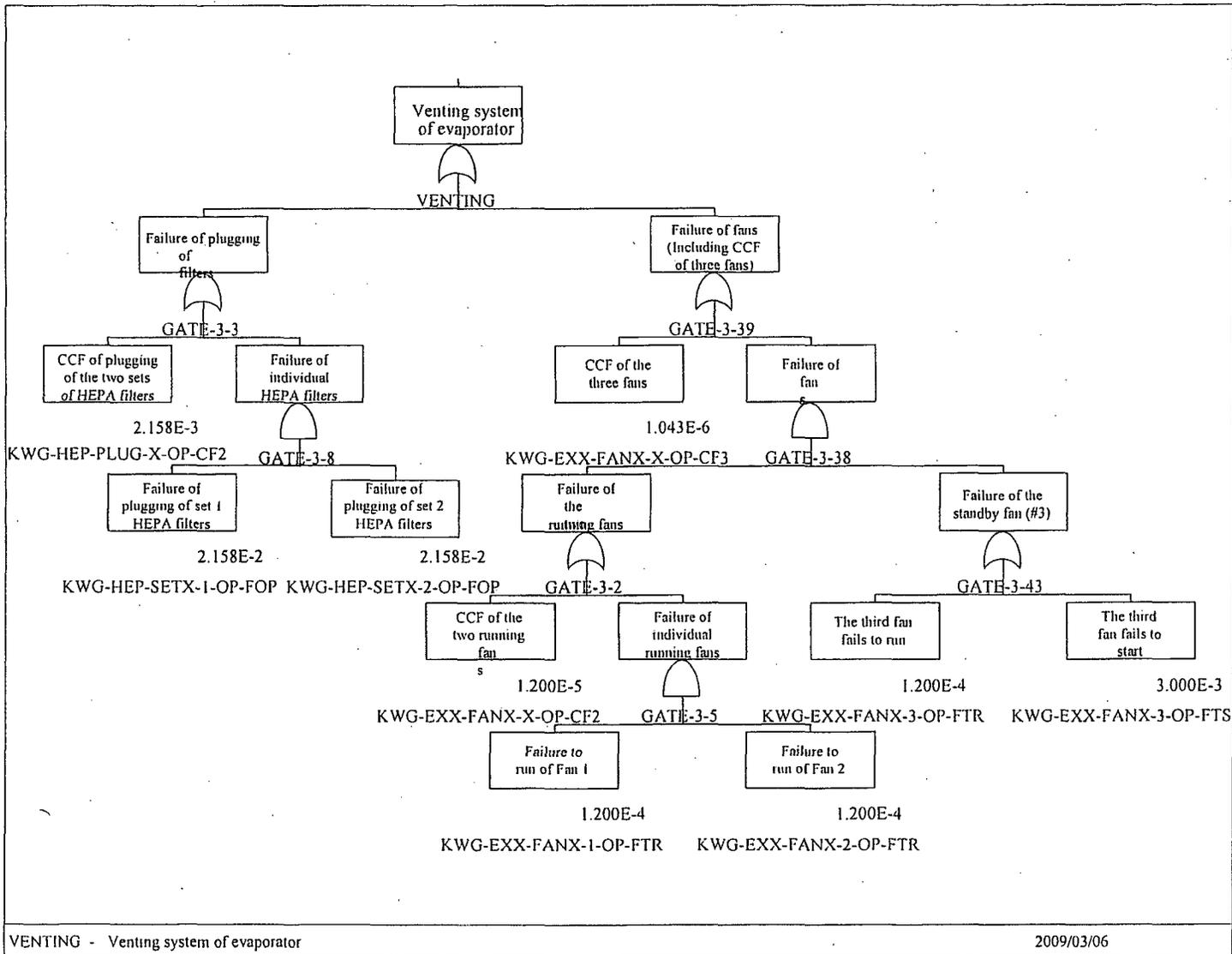


Figure A- 7: Fault Tree for Loss of Venting System

~~Official Use Only~~

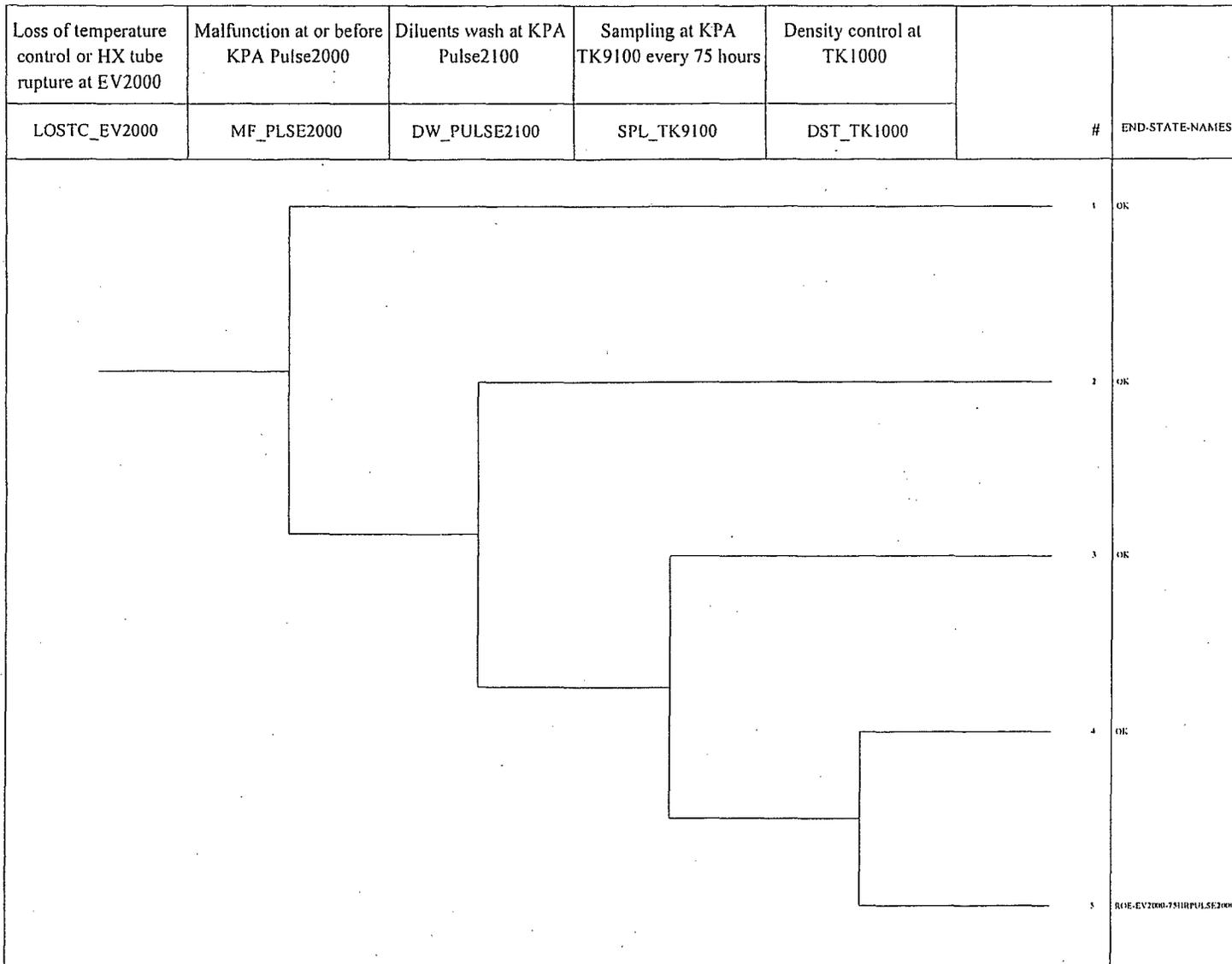


Figure A- 8: Event Tree for EV2000 ROE Scenario under Abnormal TBP Accumulation – Pathway #1 Starting from Malfunction of Pulse Column 2000

~~Official Use Only~~

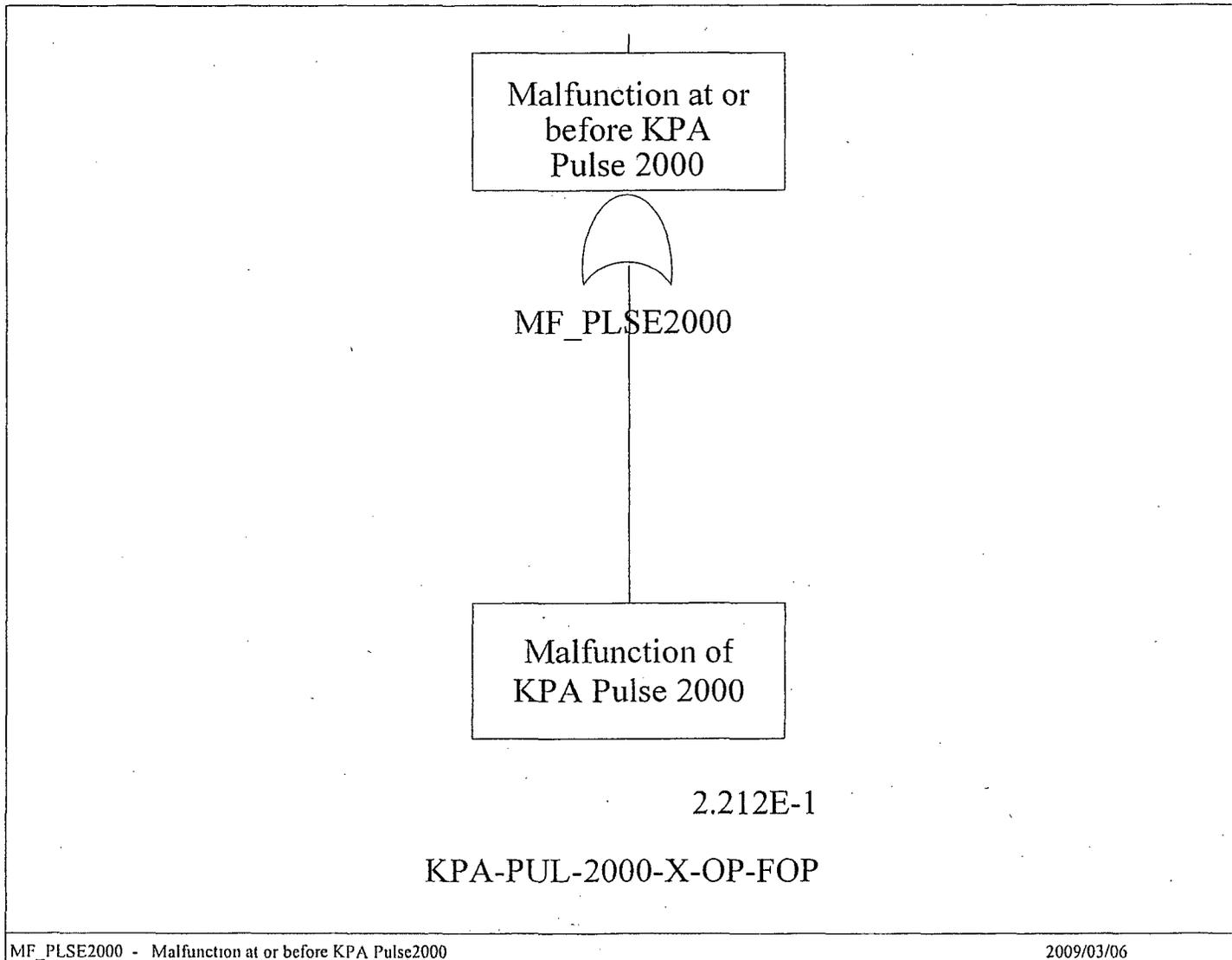


Figure A- 9: Malfunction of KPA Pulse Column 2000

~~Official Use Only~~

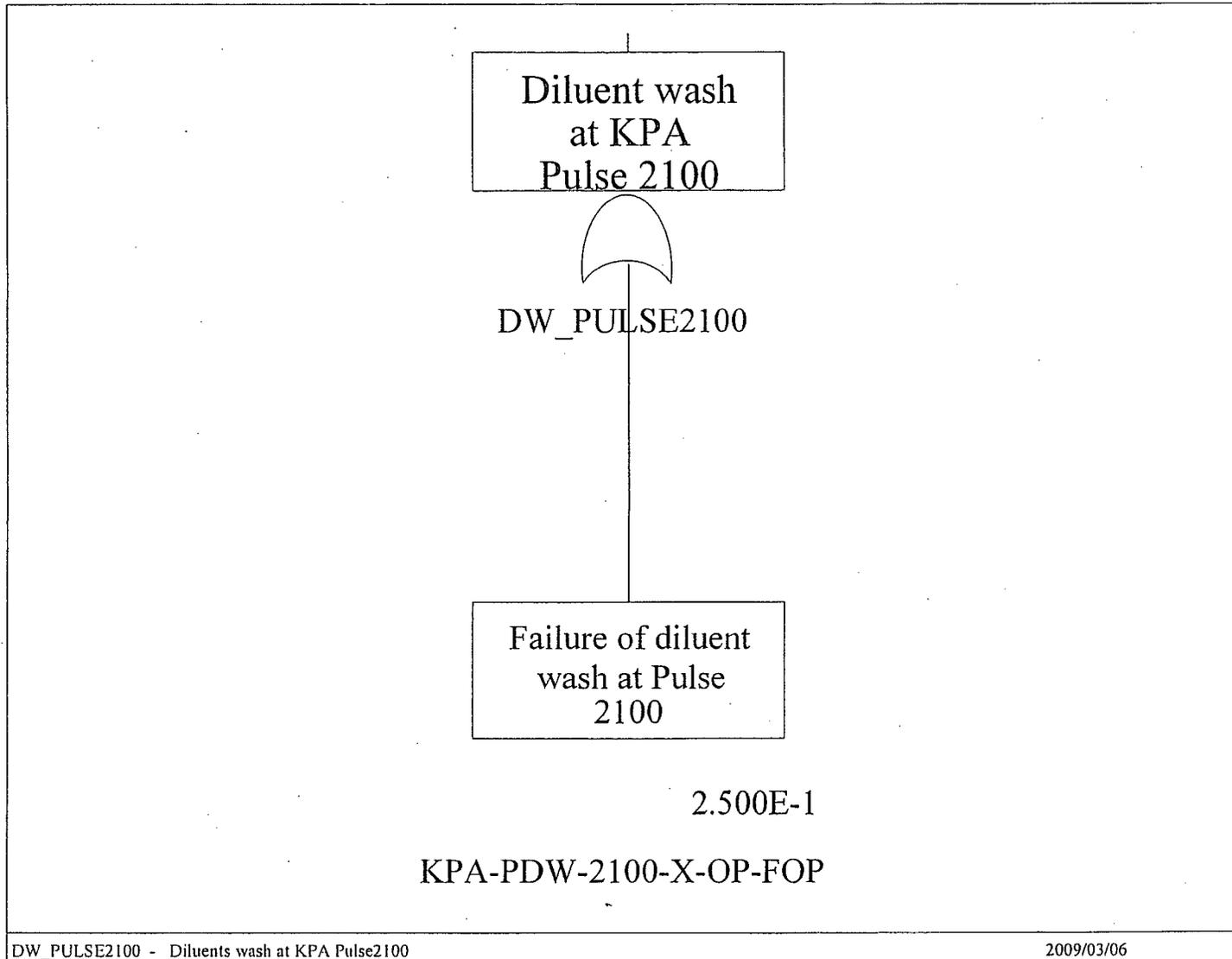


Figure A- 10: Failure of Diluent Wash at KPA Pulse Column 2100

~~Official Use Only~~

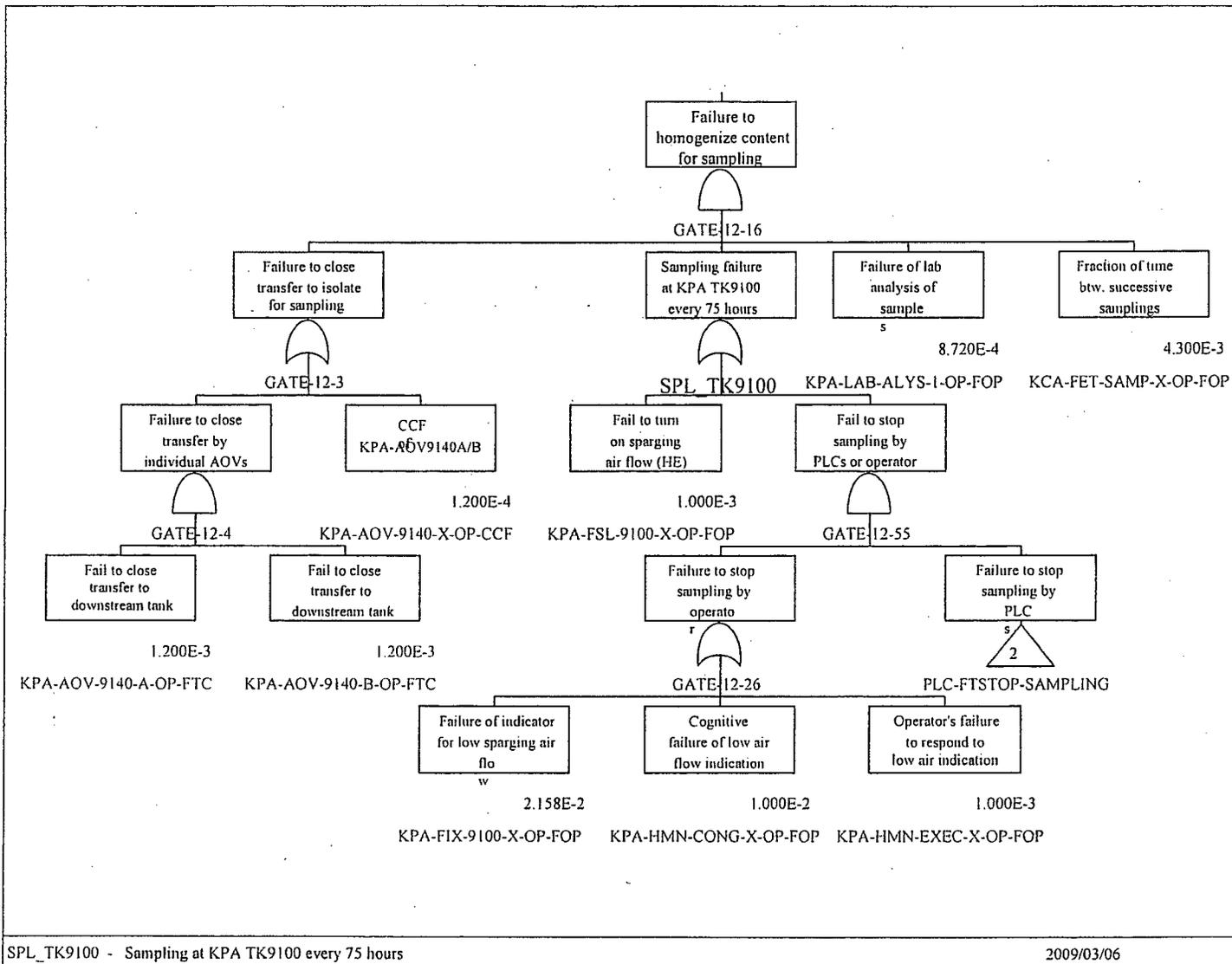


Figure A- 11: Fault Tree for Sampling at KPA TK9100 (Every 75 Hours)

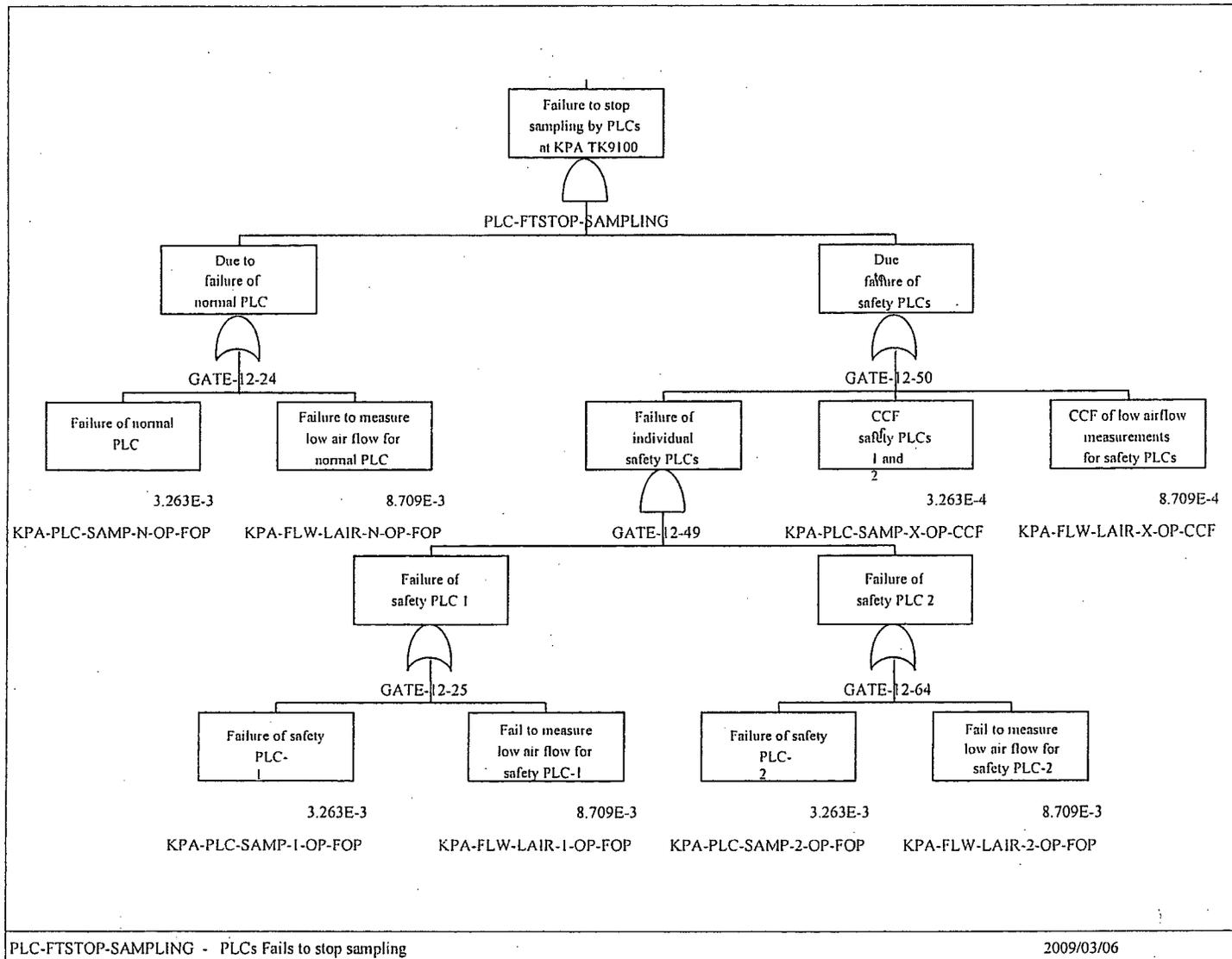


Figure A- 12: PLCs Fail to Stop Sampling at KPA TK9100

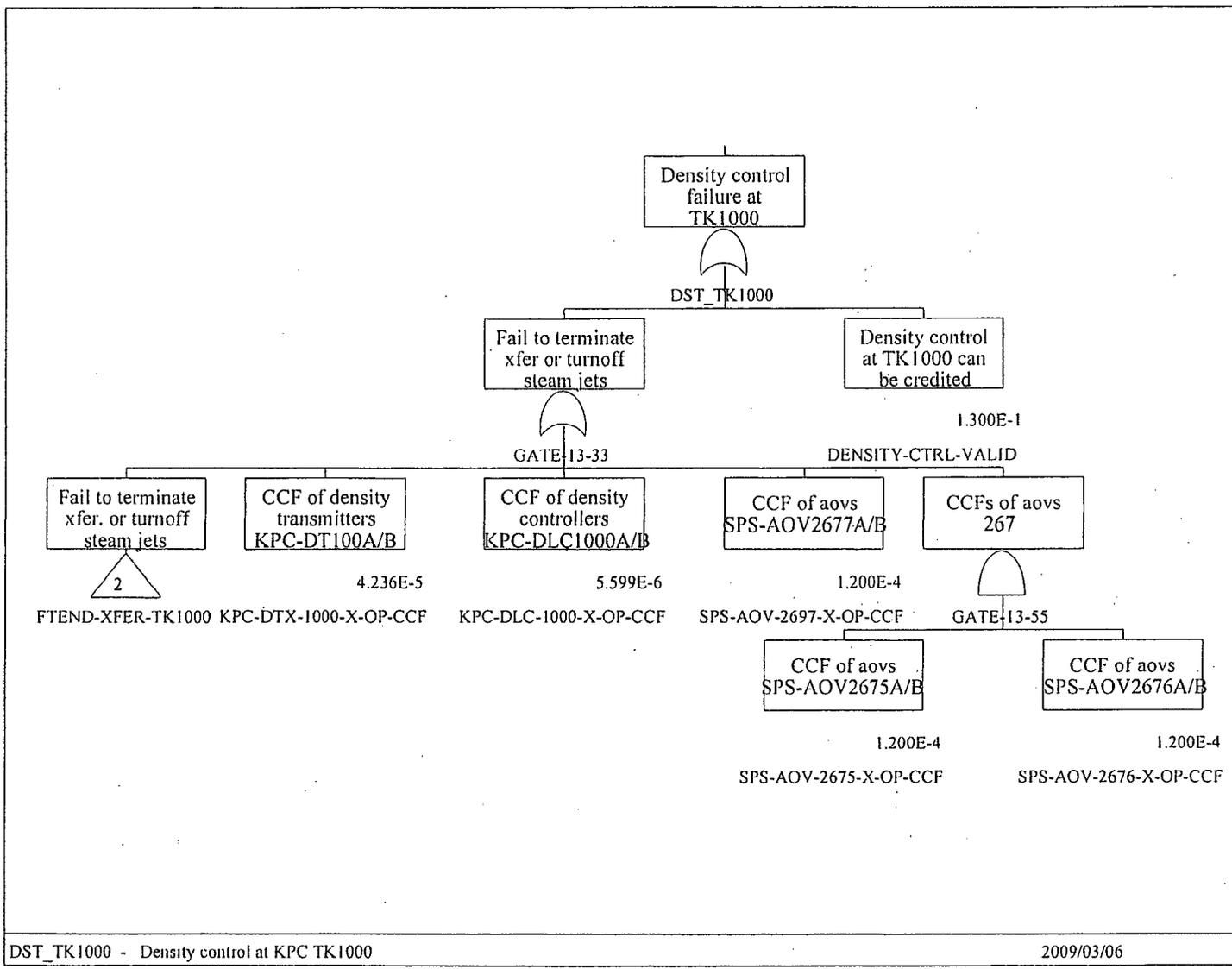
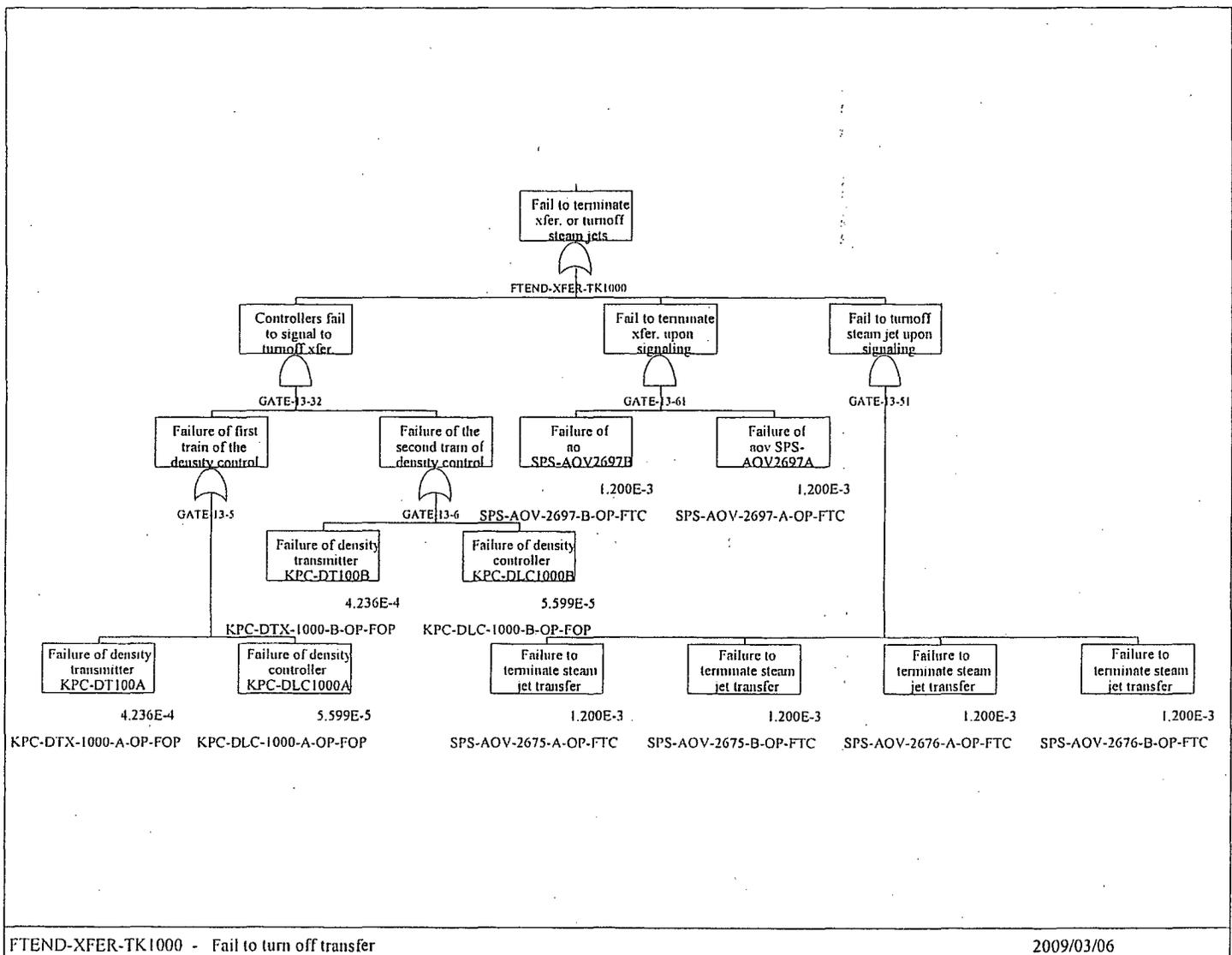


Figure A- 13: Fault Tree for Density Control at KPC TK1000 (Partially Credited for Preventing ROE) under Abnormal TBP Accumulation



FTEND-XFER-TK1000 - Fail to turn off transfer 2009/03/06

Figure A- 14: Failure to Stop Transfer or Turn off Steam Jet at TK1000

Official Use Only

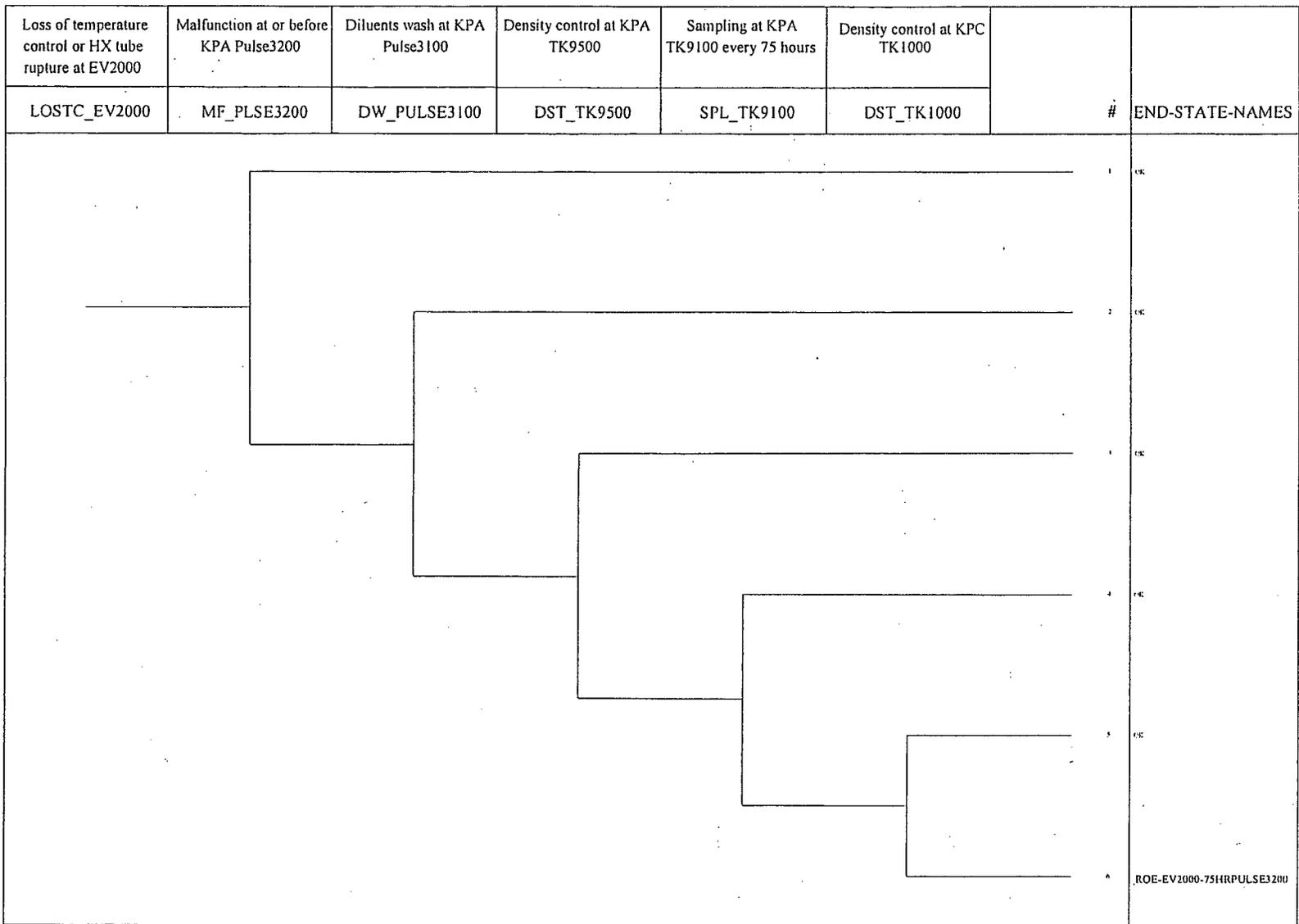


Figure A- 15: Event Tree for EV2000 ROE Scenario under Abnormal TBP Accumulation – Pathway #2 Starting from Malfunction of Pulse Column 3200

Official Use Only

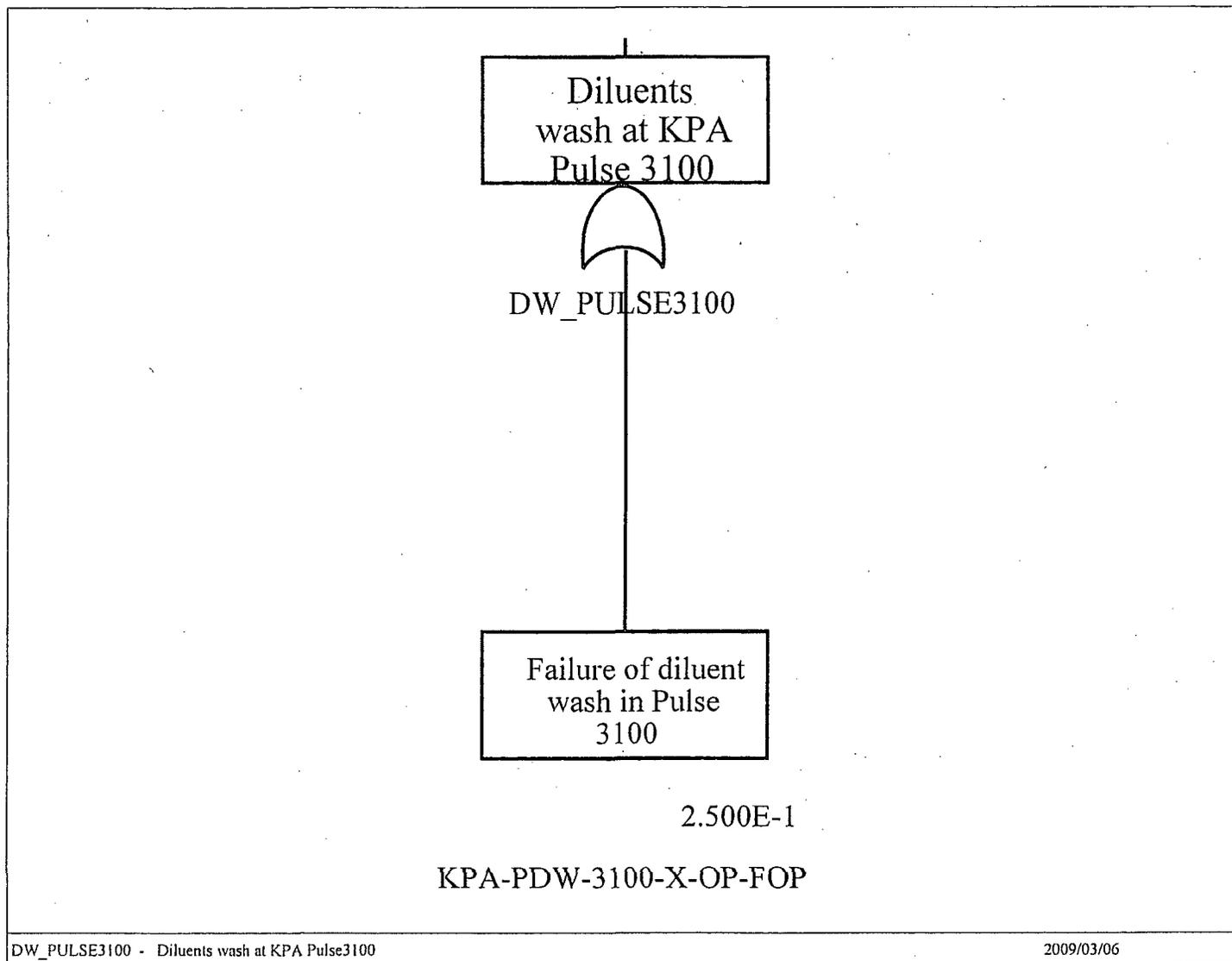


Figure A- 16: Malfunction of Diluent Wash at KPA Pulse Column 3100

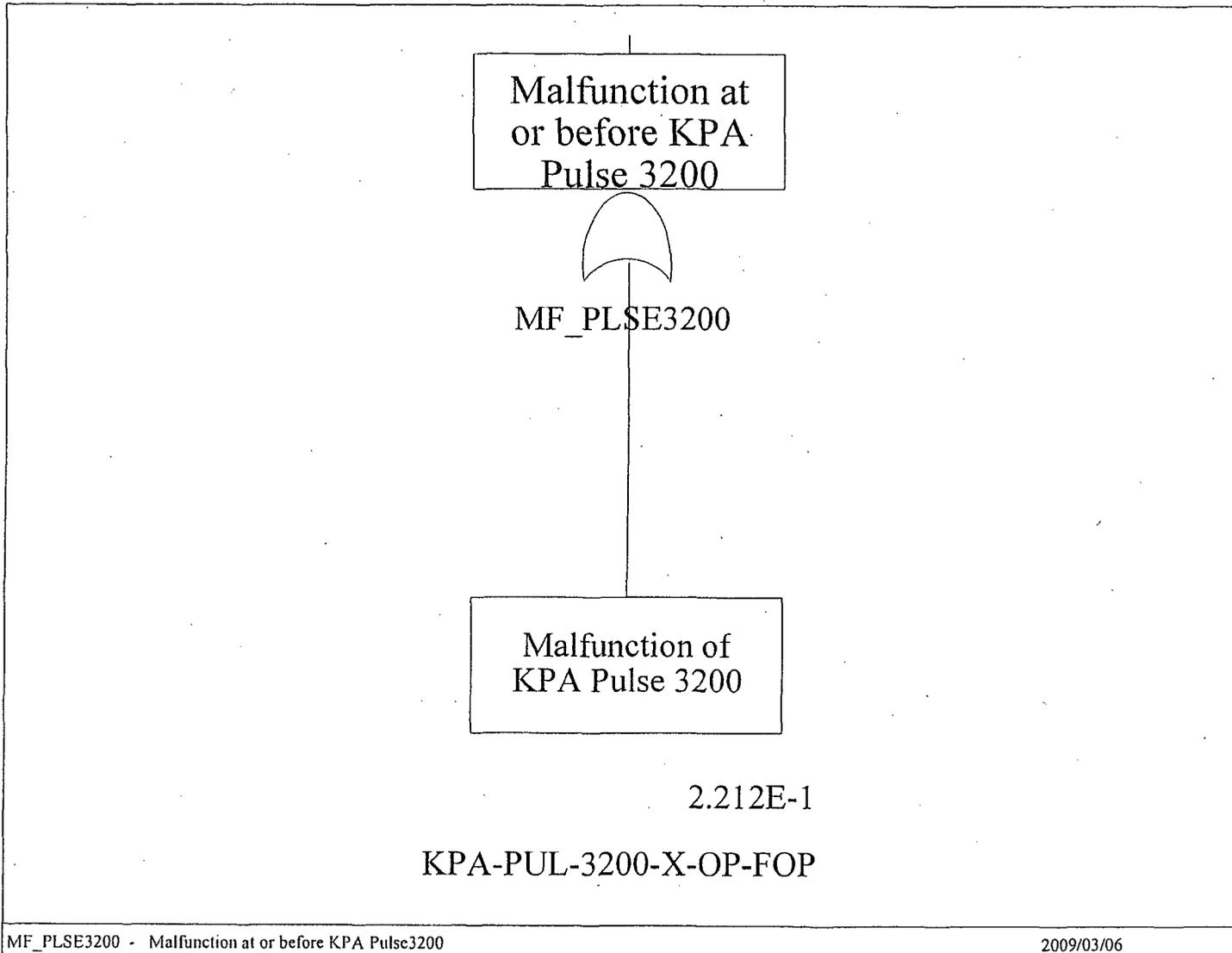


Figure A- 17: Malfunction of KPA Pulse Column 3200

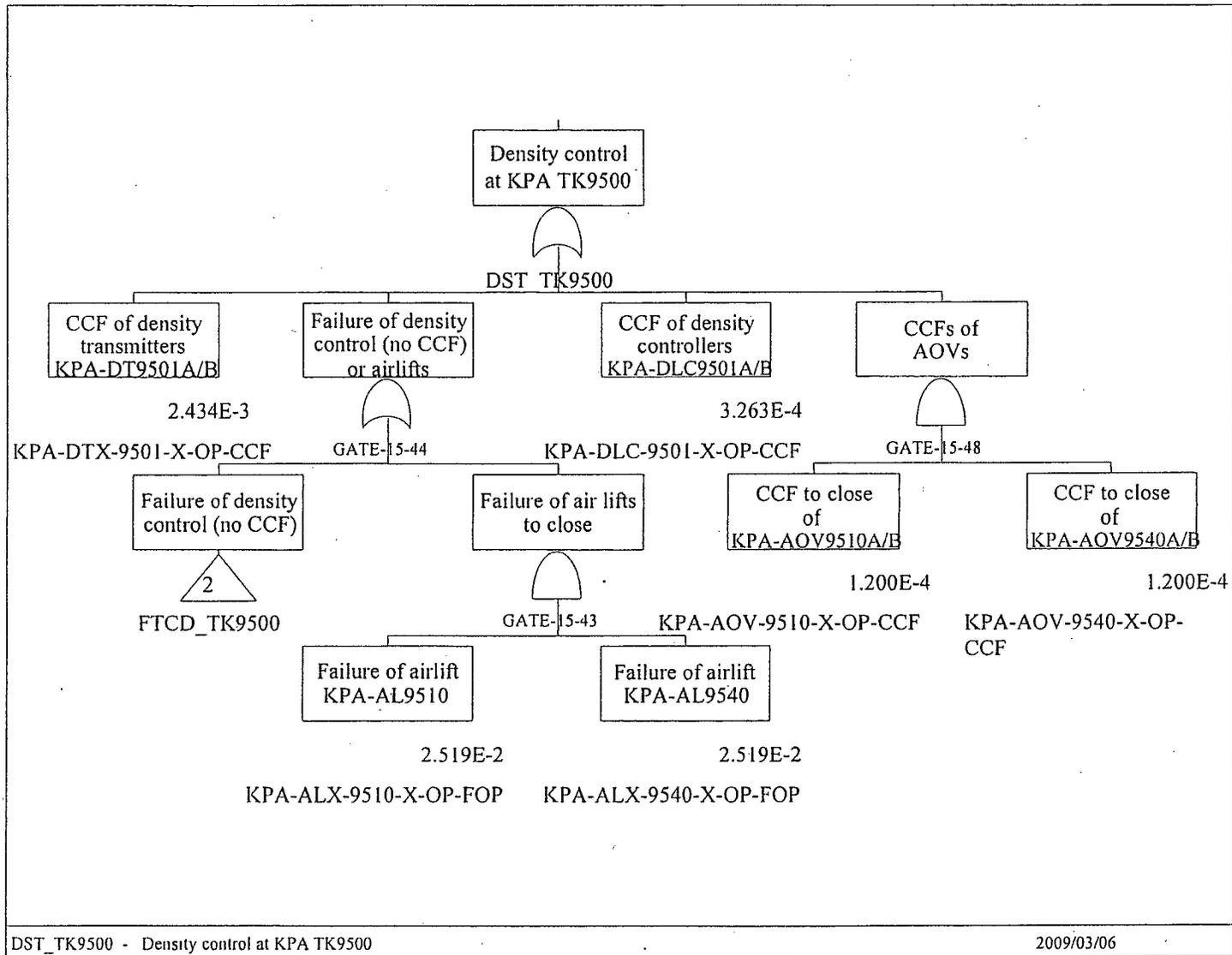


Figure A- 18: Fault Tree for Density Control at KPA TK9500

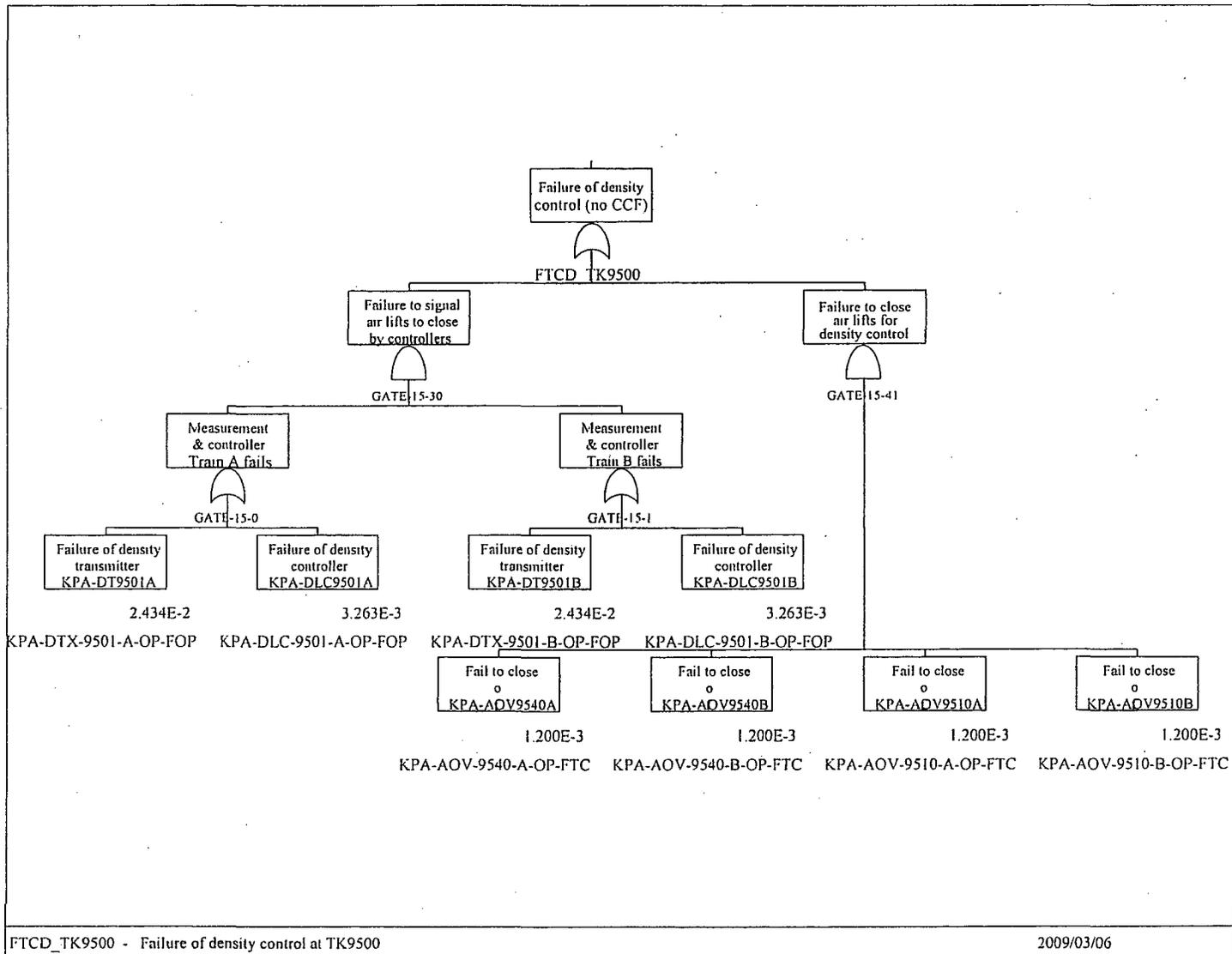


Figure A- 19: Failure of Density Control at KPA TK9500

Official Use Only

Loss of cooling or mixing at TK3000	Level control or no excessive TBP at TK3000	Venting system of evaporator			
LOSC_M_TK3000	L_TBP-TK3000	VENTING	#	END-STATE-NAMES	
<pre>graph LR; A[Normal condition] --> B1[]; B1 --> C1[]; C1 --> D1[OK]; A --> B2[]; B2 --> C2[]; C2 --> D2[ROE-TK3000-1-NC]; A --> B3[]; B3 --> C3[]; C3 --> D3[ROE-TK3000-2-NC];</pre>					

Figure A- 20: Event Tree for ROE Scenario under Normal TBP Accumulation for TK3000

Official Use Only

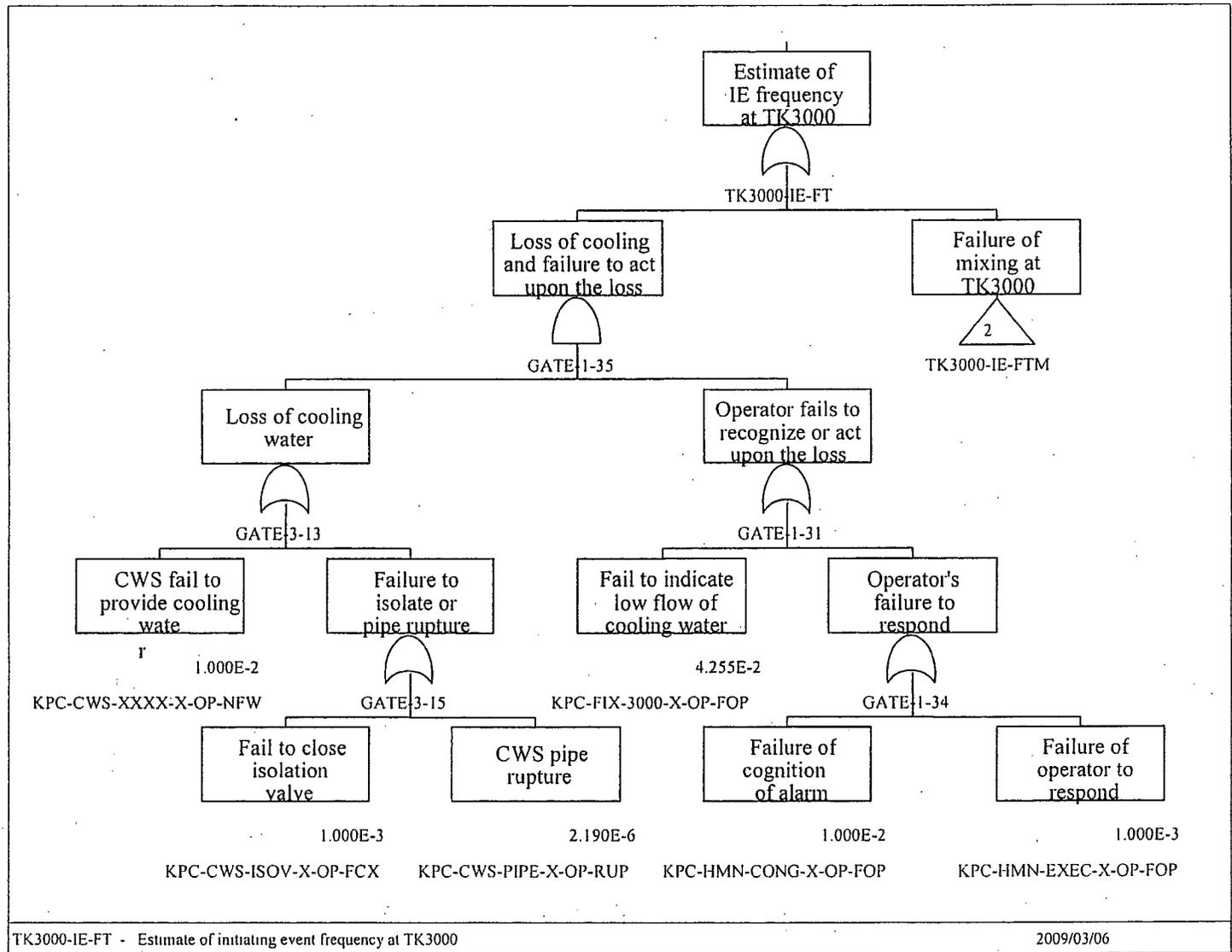


Figure A- 21: Fault Tree for Initiating Event of TK3000 Scenario

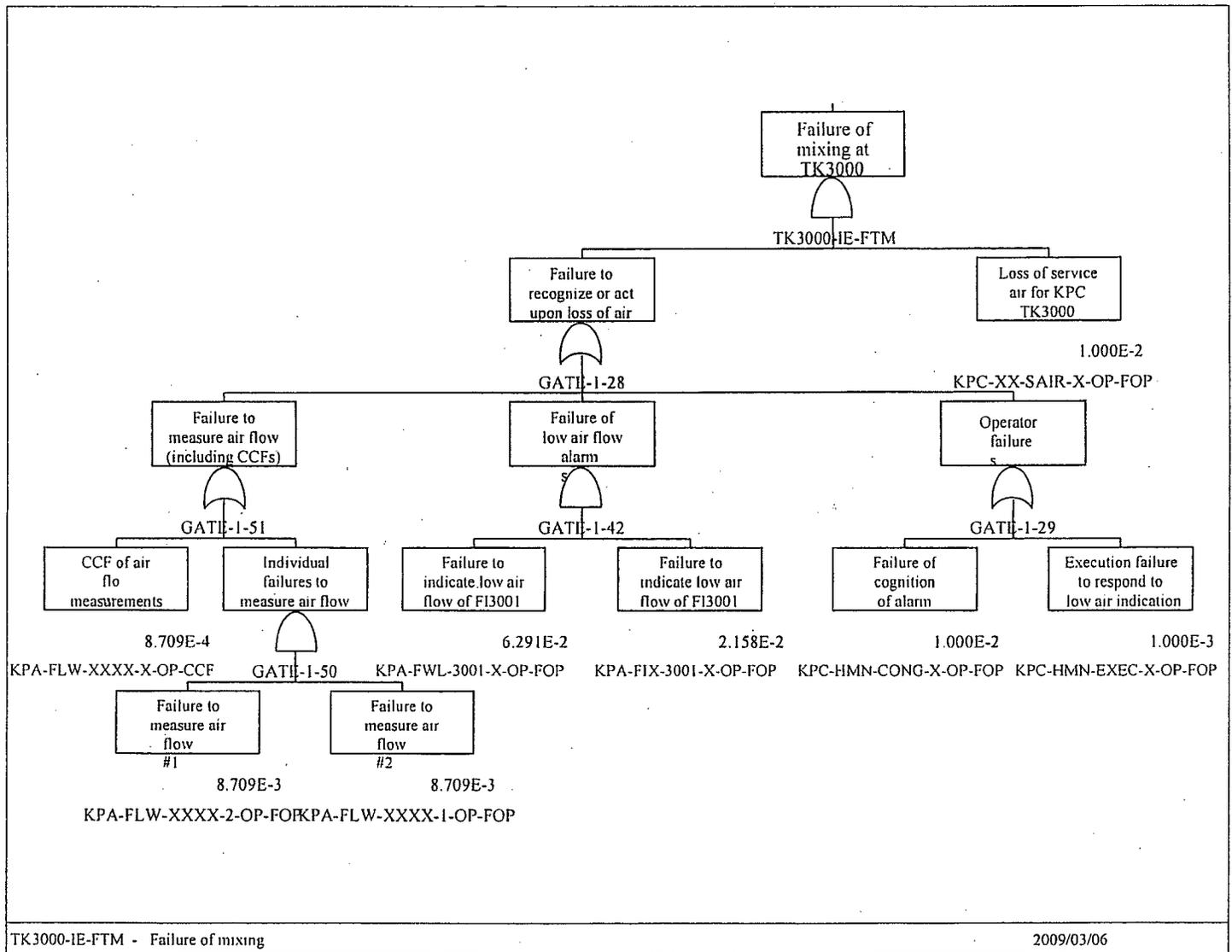


Figure A- 22: Failure of Mixing at TK3000

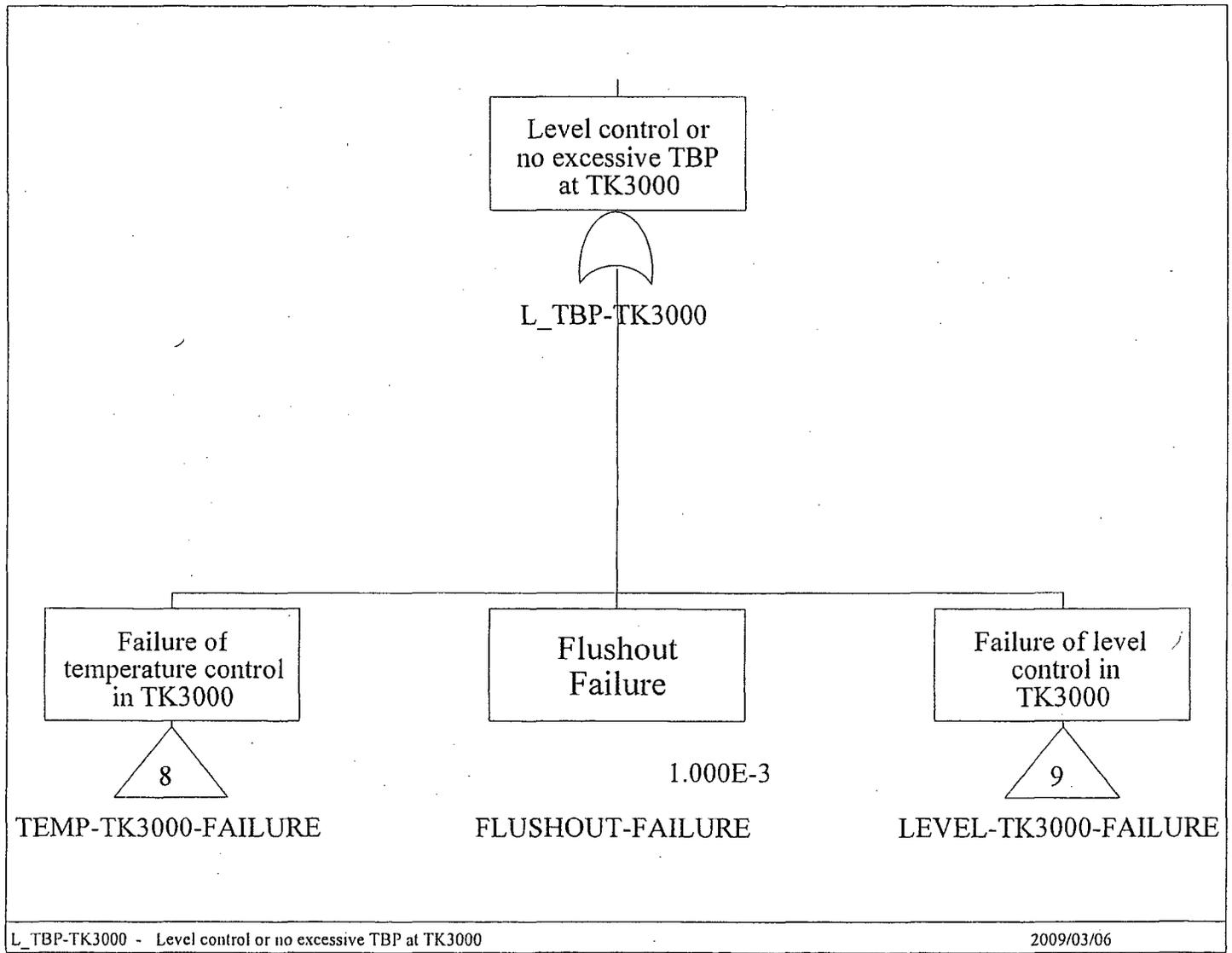


Figure A- 23: Fault Tree for Loss of Evaporative Cooling due to Failure of Temperature or Level Control

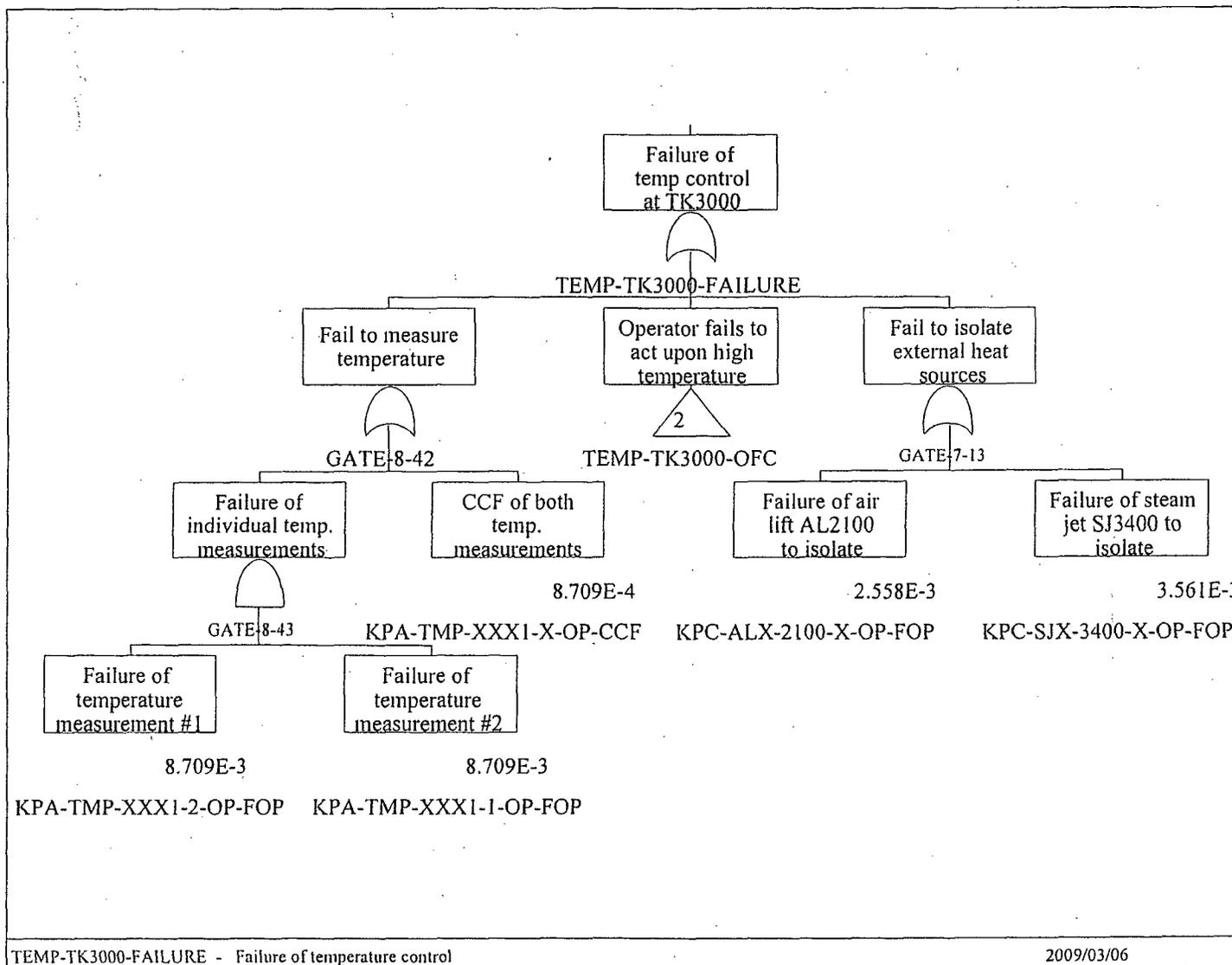


Figure A- 24: Fault Tree for Loss of Temperature Control at TK3000

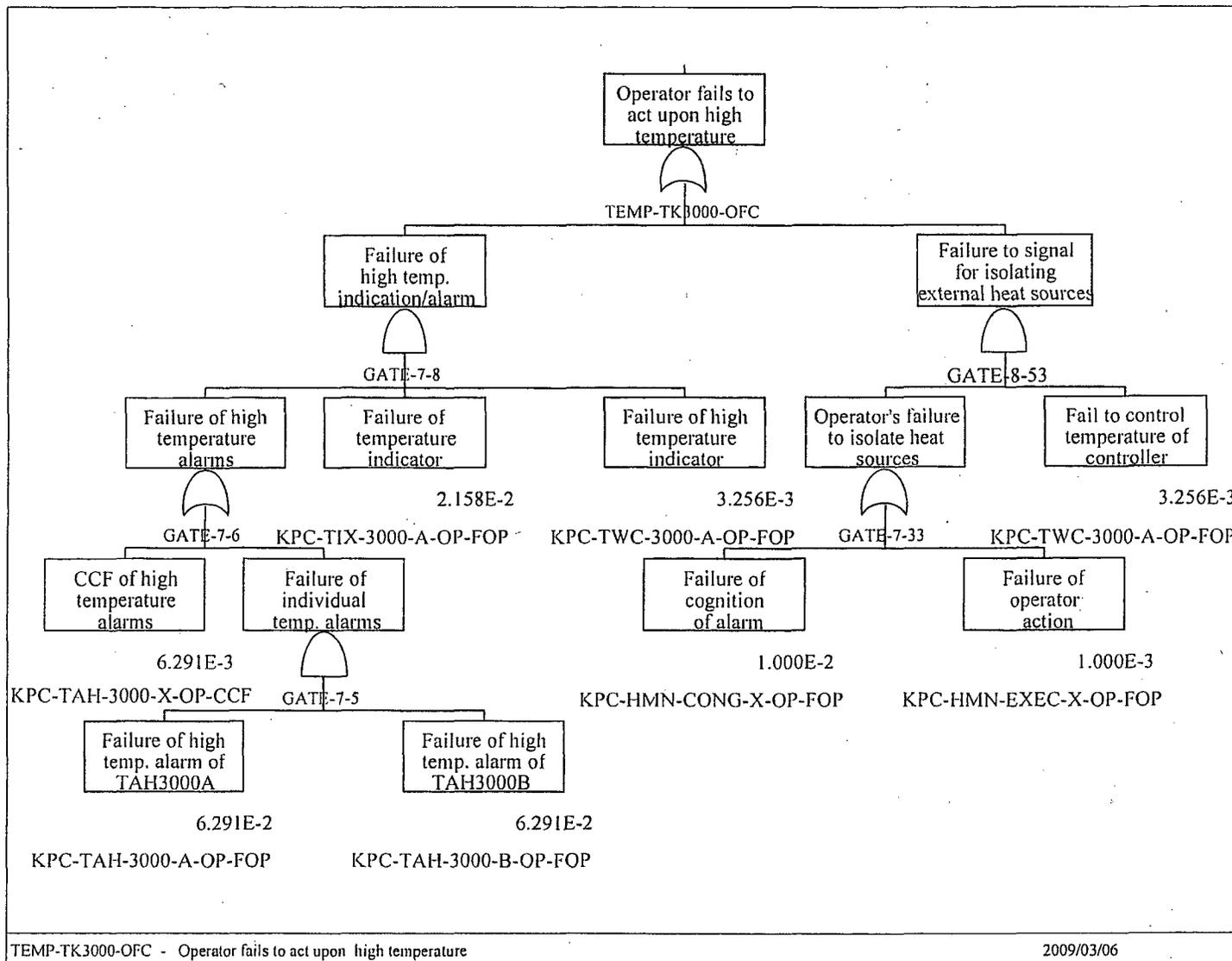


Figure A- 25: Fault Tree for Operator's Failure to Act upon High Temperature at TK3000

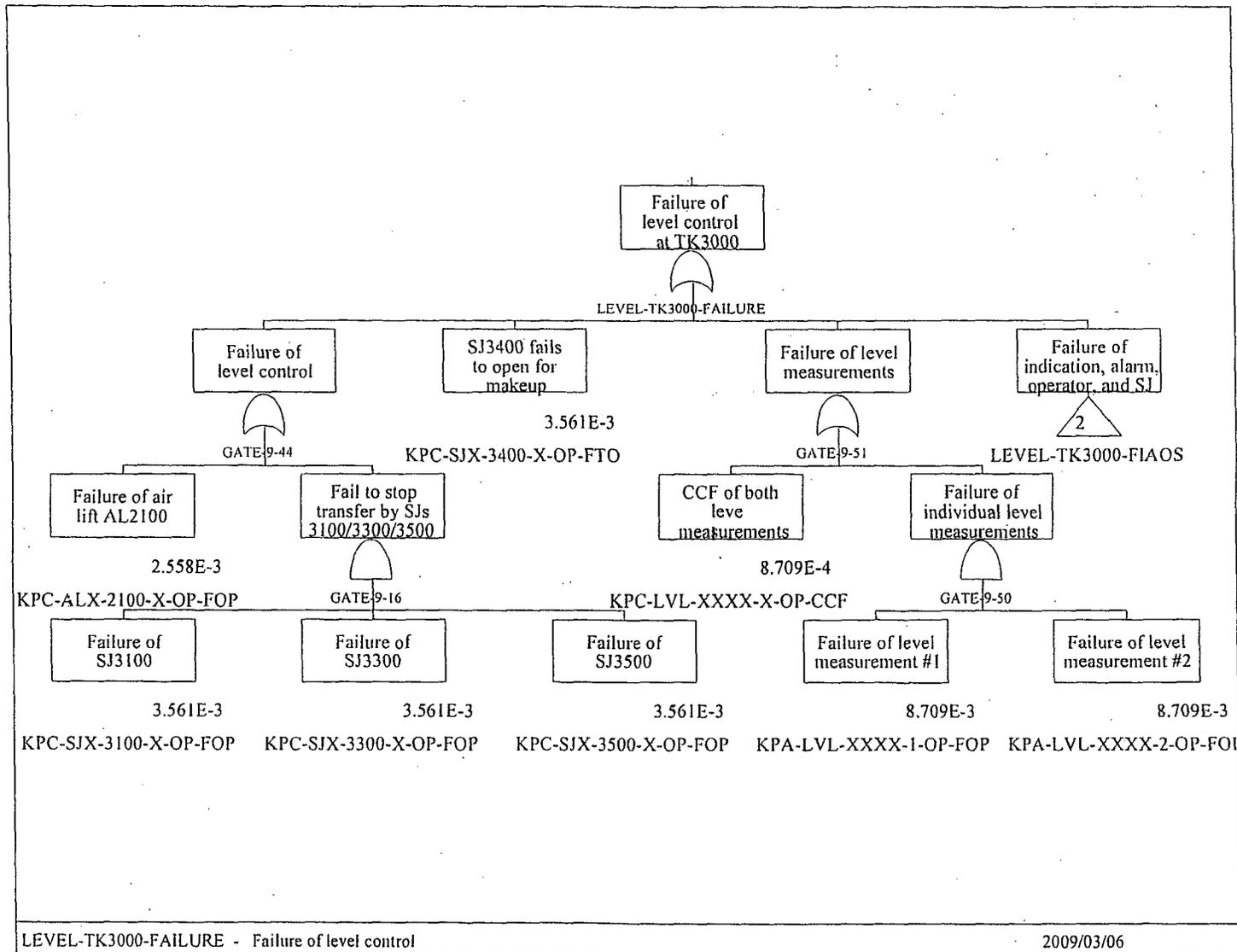


Figure A- 26: Fault Tree for Loss of Level Control at TK3000

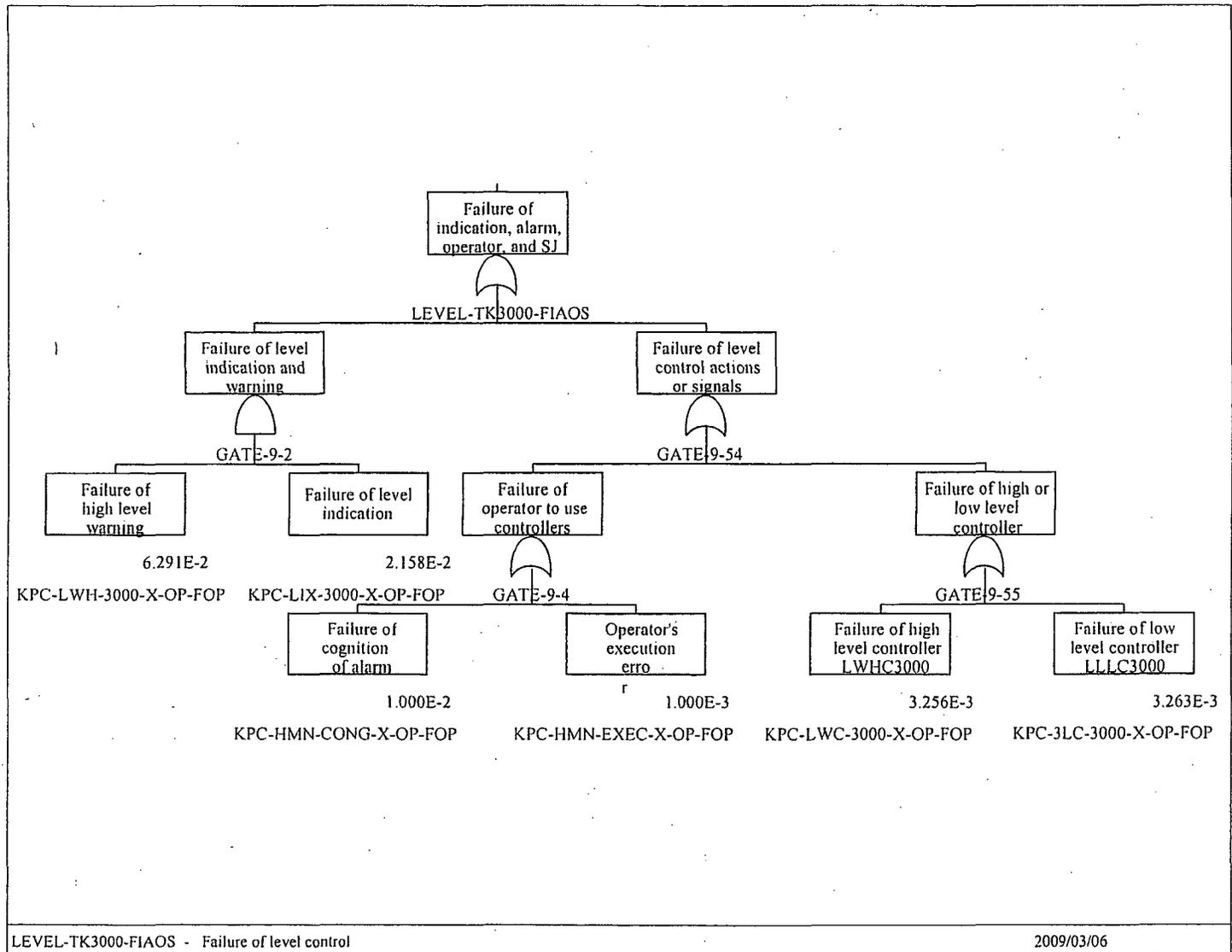


Figure A- 27: Failure of Indication, Alarm, Operator's Actions, and Steam Jet for Makeup in TK3000

~~Official Use Only~~

Loss of cooling or mixing at TK3000	Malfunction at or before KPA Pulse2000	Diluents wash at KPA Pulse2100	Sampling at KPA TK9100 every 75 hours	Density control at TK1000		
LOSC_M_TK3000	MF_PLSE2000	DW_PULSE2100	SPL_TK9100	DST_TK1000	#	END-STATE-NAMES
					1	OK
					2	OK
					3	OK
					4	OK
					5	ROE-TK3000-PULSE2000

Figure A-28: Event Tree for ROE Scenario at TK3000 under Abnormal TBP Accumulation - Pathway #1 Starting from Malfunction of Pulse 2000

~~Official Use Only~~

Official Use Only

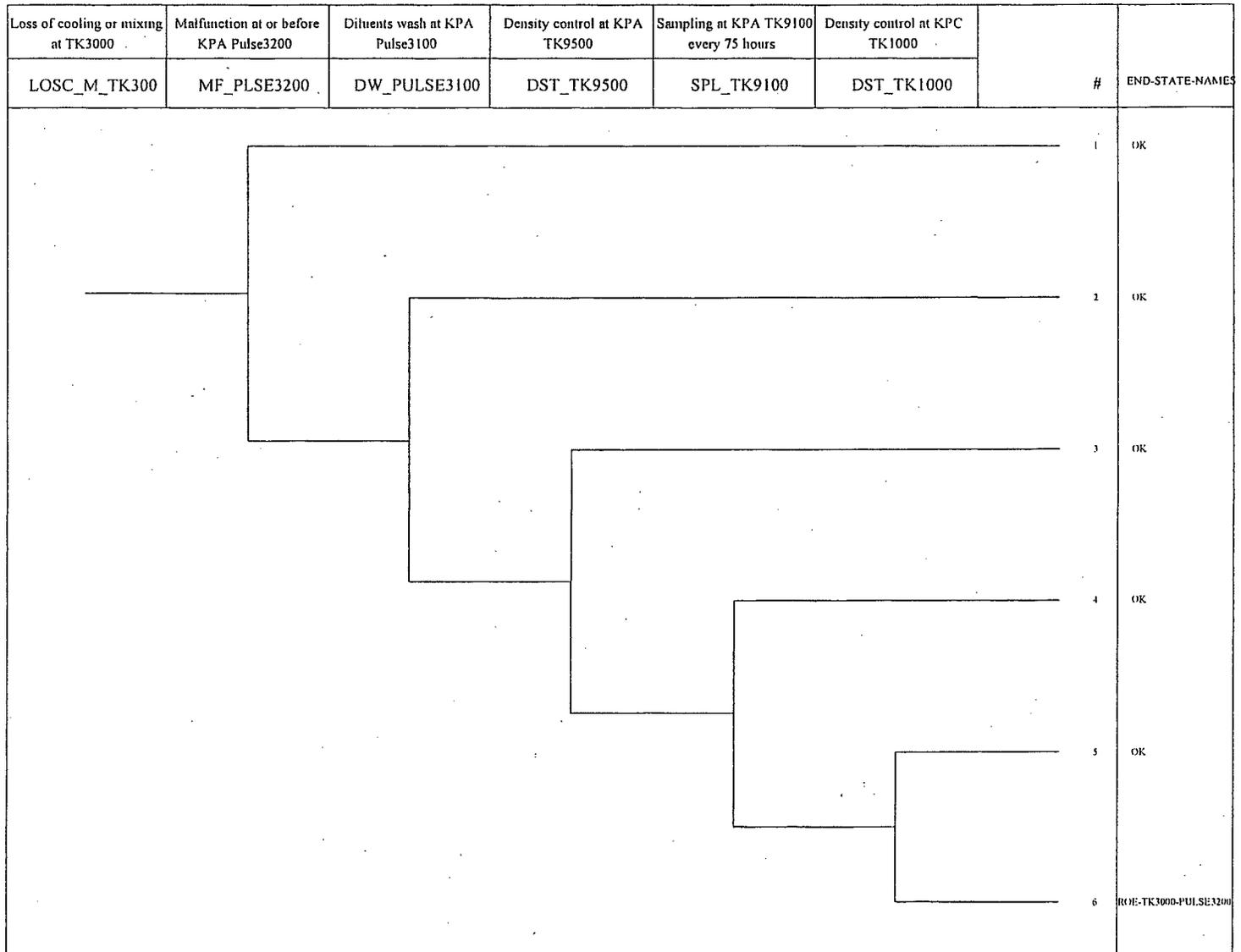


Figure A- 29: Event Tree for ROE Scenario at TK3000 under Abnormal TBP Accumulation – Pathway #2 Starting from Malfunction of Pulse 3200

Official Use Only

Official Use Only

Solvent transfer and mechanical entrainment	Malfunction of KPA Pulse 3100 diluent wash	Failure of slab settler	Failure of sampling in KCA batch tank		
IE-STME	DWKPA_PLSE3100	MF_SLAB	FSPL_KCA_BT	#	END-STATE-NAMES
<pre>graph LR; A[IE-STME] --> B[DWKPA_PLSE3100]; B --> C[MF_SLAB]; C --> D[FSPL_KCA_BT]; D --> E[ROE-EV3000-STME];</pre>				1	OK
				2	OK
				3	OK
				4	ROE-EV3000-STME

Figure A- 30: Event Tree for ROE in KCD EV3000 due to Solvent Transferred by Mechanical Entrainment

Official Use Only

Official Use Only

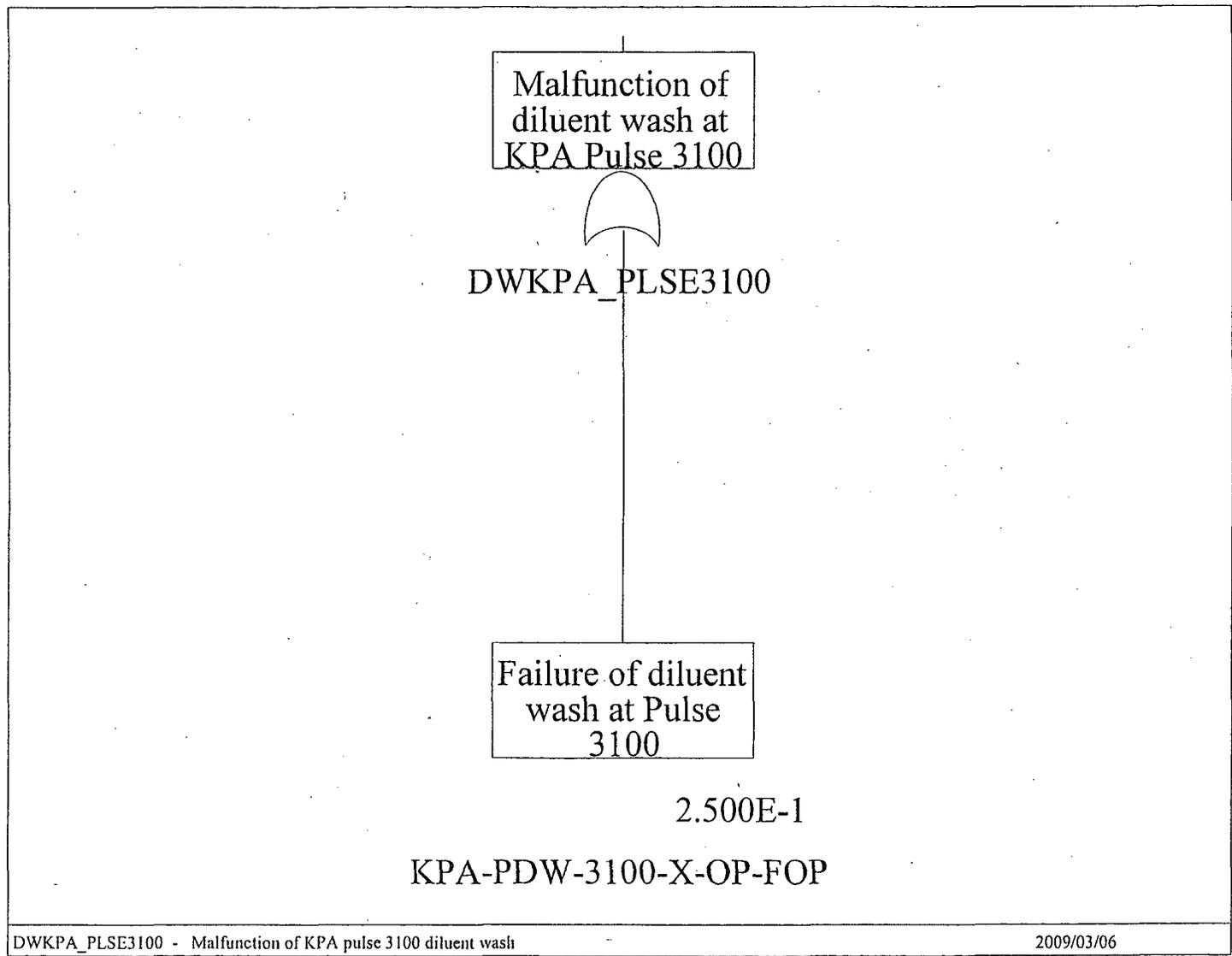


Figure A- 31: Fault Tree for Failure of Diluent Wash at Pulse 3100

Official Use Only

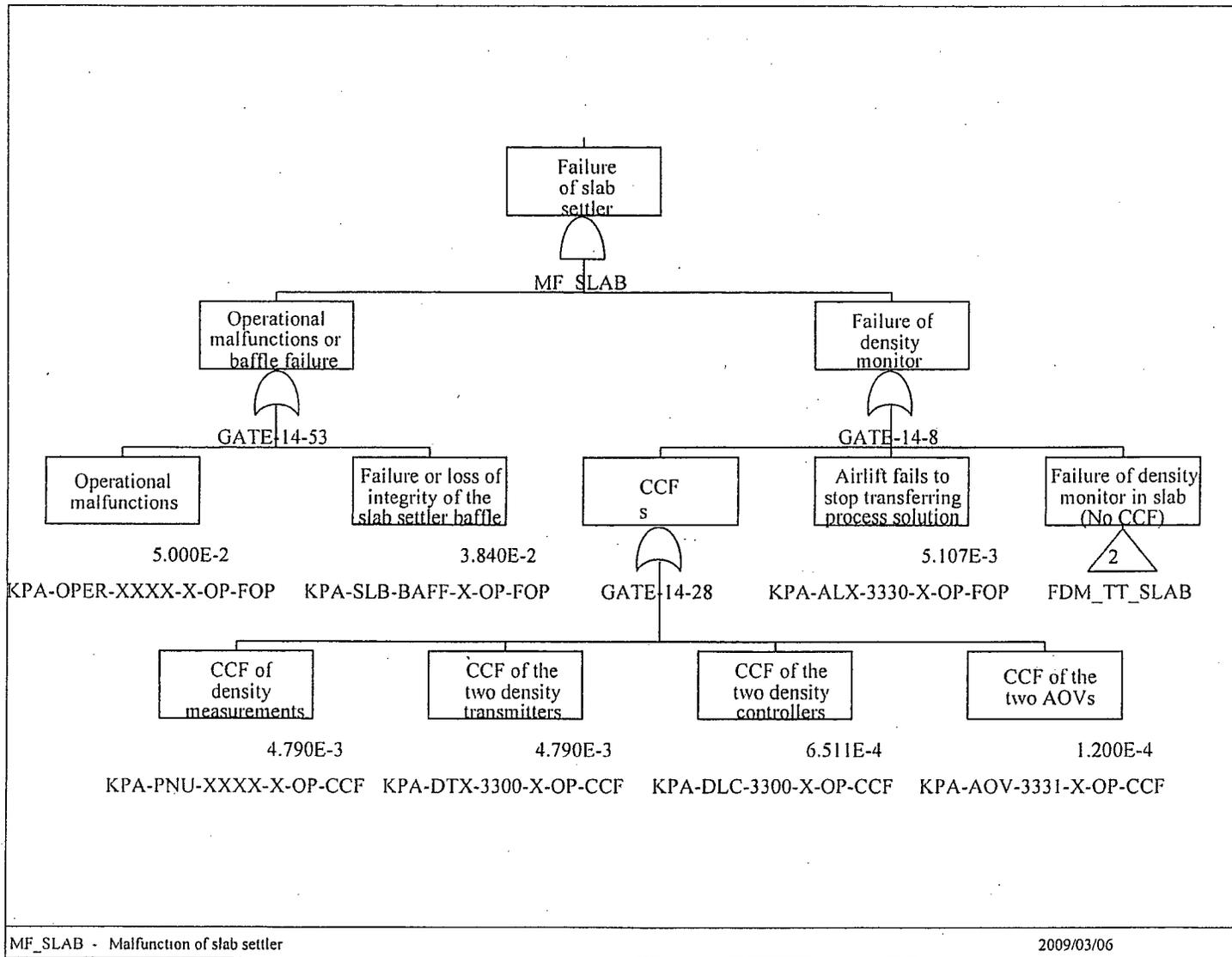


Figure A-32: Fault Tree for Malfunction of Slab Settler

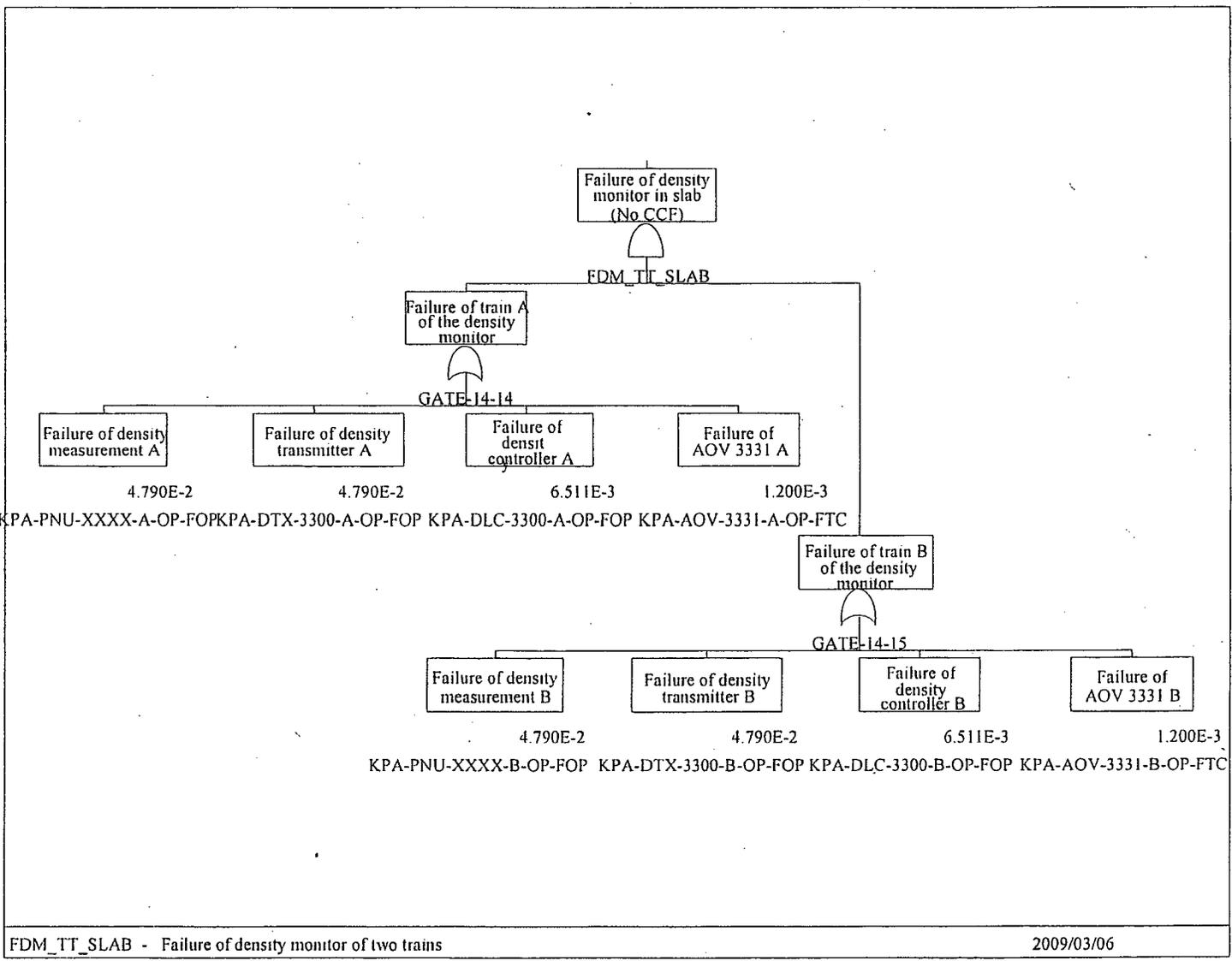


Figure A- 33: Failure of Density Monitor in Slab Settler

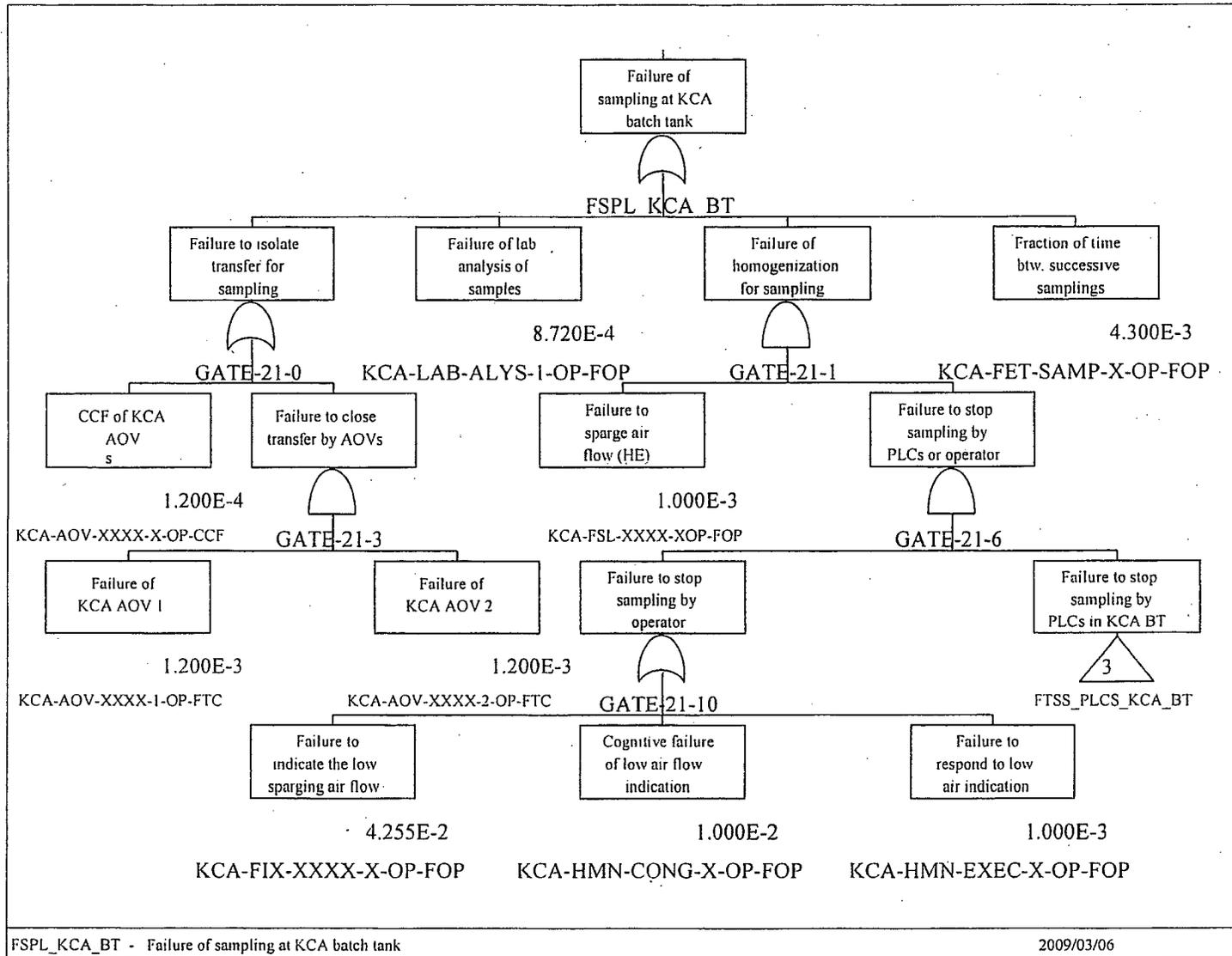


Figure A- 34: Fault Tree for Failure of Sampling at KCA Batch Tank (BT)

Official Use Only

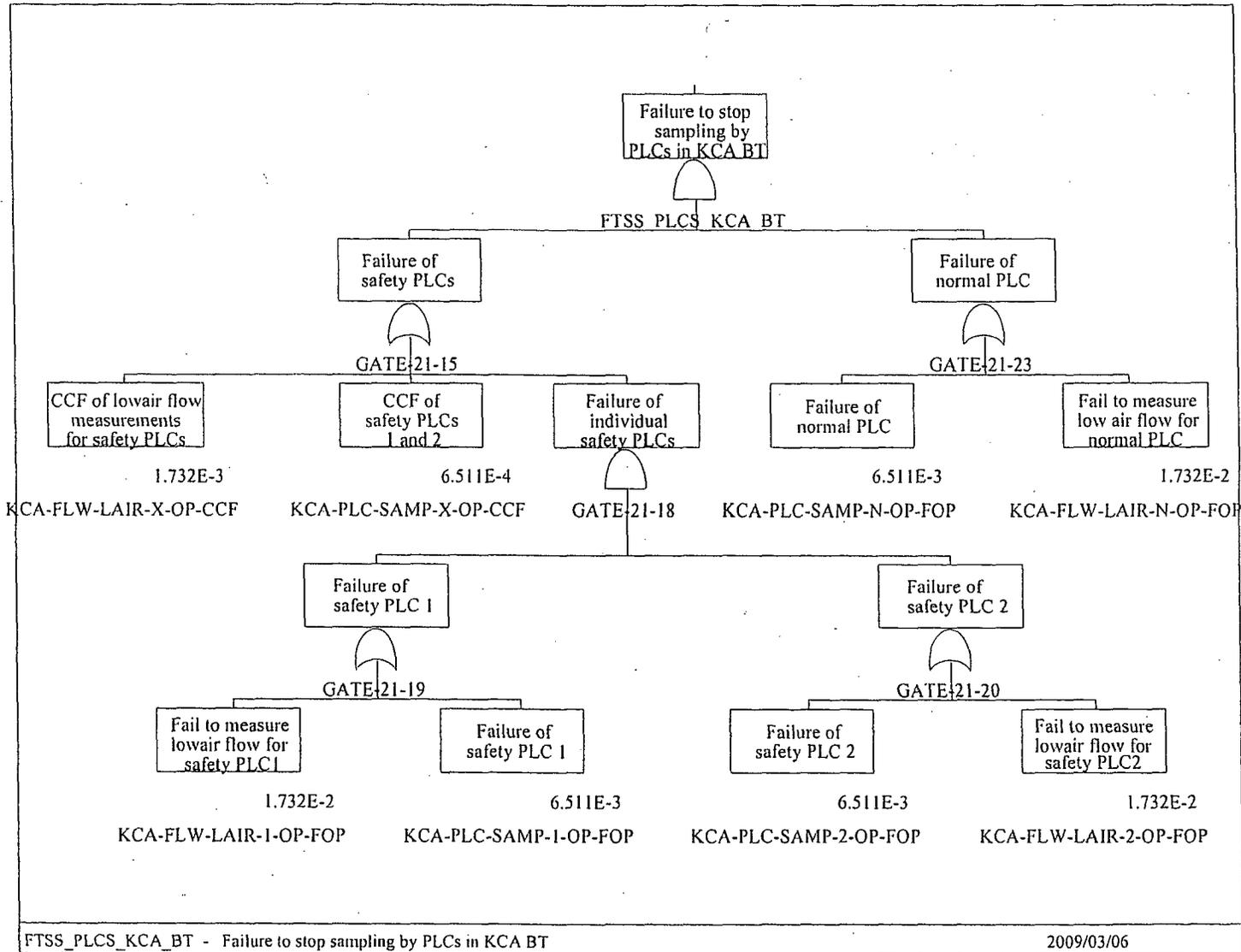


Figure A-35: Failure of PLCs to Stop Sampling at KCA Batch Tank (BT)

Official Use Only

~~Official Use Only~~

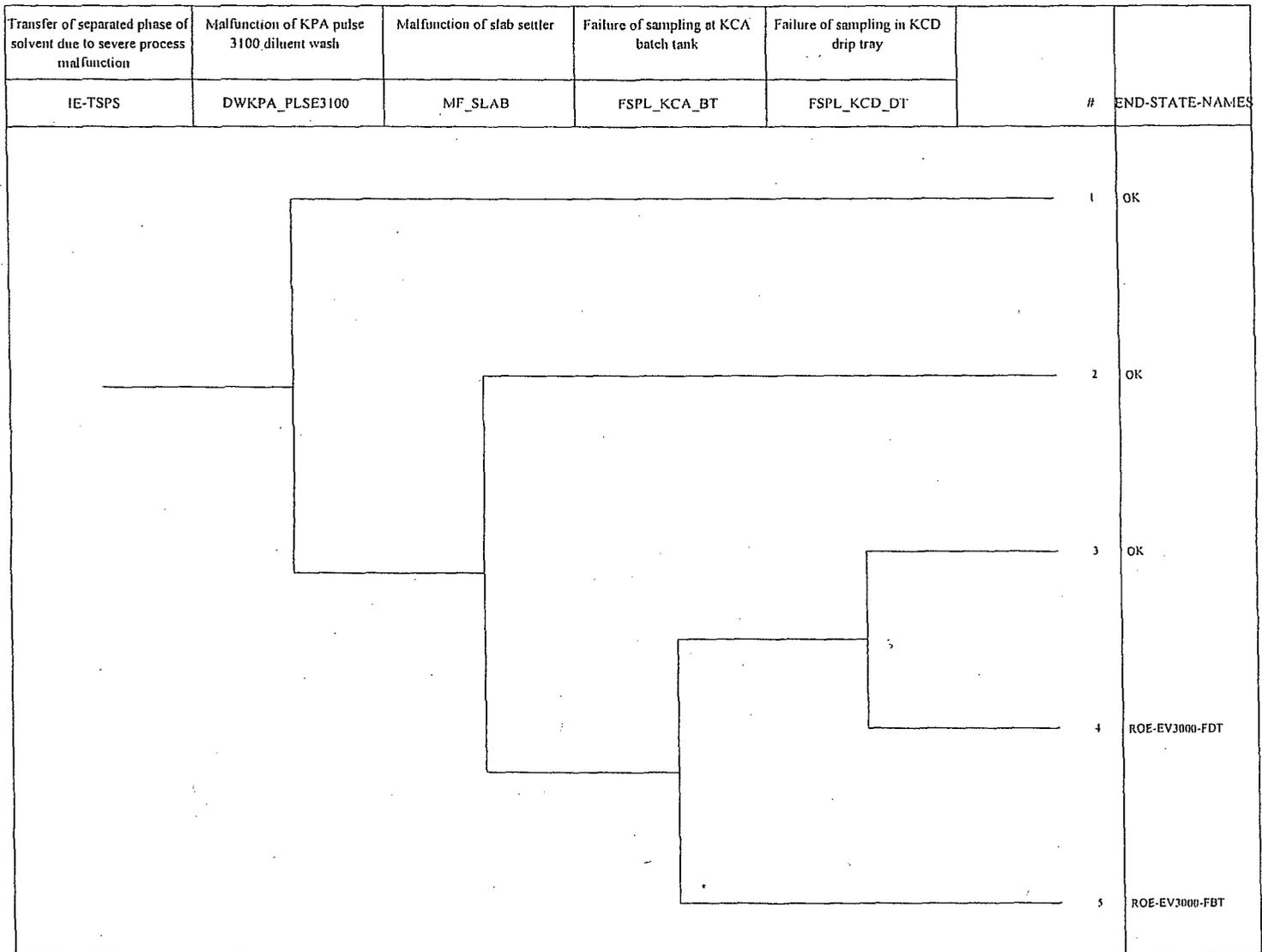


Figure A- 36: Event Tree for ROE in KCD EV3000 due to Transfer of Separated Phase of Solvent due to Severe Process Malfunction

~~Official Use Only~~

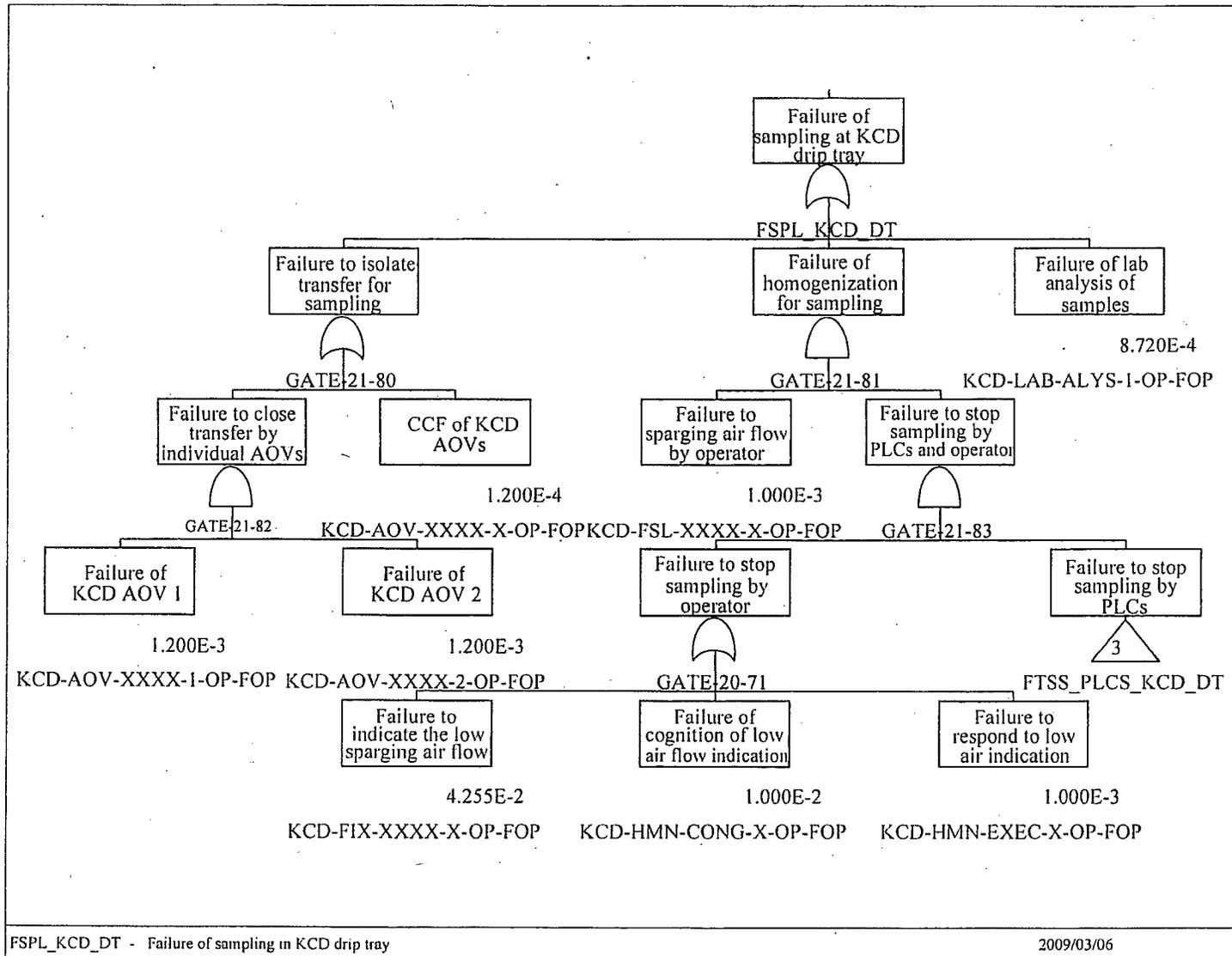


Figure A-37: Fault Tree for Failure of Sampling at KCD Drip Tray (DT)

Official Use Only

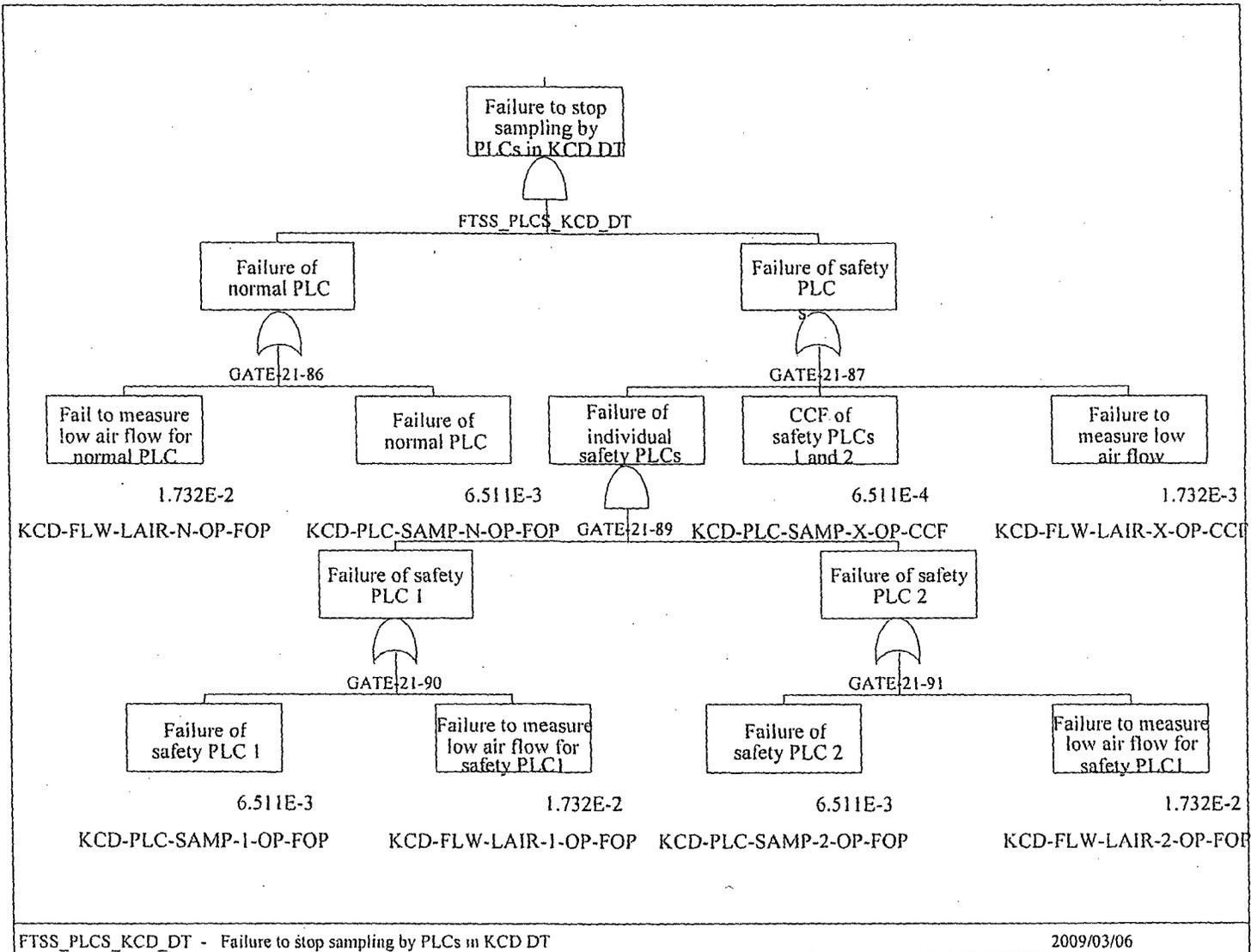


Figure A-38: Failure of PLCs to Stop Sampling in KCD Drip Tray (DT)

Official Use Only

APPENDIX B

**RED OIL SAFETY STRATEGY AND TBP PREVENTION STRATEGY BY
VESSEL IN THE AP PROCESS UNITS**

Table B-1: Red Oil Safety Strategy by Vessel

Vessel	TBP Present (Normal Condition)	TBP Present (Upset/ Separate Condition)	General Safety Strategy
KCA Unit			
KCA*FLT7000	N	N	PREVENTION
KCA*FUR8000	N	N	PREVENTION
KCA*PREC5000	N	N	PREVENTION
KCA*PREC6000	N	N	PREVENTION
KCA*TK1000	N	N	PREVENTION
KCA*TK2000	N	N	PREVENTION
KCD Unit			
KCD*EV3000	N	N	PREVENTION
KCD*TK1000	N	N	PREVENTION
KCD*TK1500	N	N	PREVENTION
KCD*TK2000	N	N	PREVENTION
KCD*TK4000	N	N	PREVENTION
KCD*TK4100	N	N	PREVENTION
KCD*TK4200	N	N	PREVENTION
KCD*TK6000	N	N	PREVENTION
KCD*TK7000	N	N	PREVENTION
KCD*TK7500	N	N	PREVENTION
KPA Unit			
KPA*CLMN6000	N	N	PREVENTION
KPA*CLMN6500	N	N	PREVENTION
KPA*MIX4000	Y		HEAT TRANSFER
KPA*MIX5000	Y		HEAT TRANSFER
KPA*MIX5100	N	Y	HEAT TRANSFER
KPA*PULS2000	Y		HEAT TRANSFER
KPA*PULS2100	N	Y	HEAT TRANSFER
KPA*PULS2200	Y		HEAT TRANSFER
KPA*PULS3000	Y		HEAT TRANSFER
KPA*PULS3100	N	Y	HEAT TRANSFER
KPA*PULS3200	Y		HEAT TRANSFER
KPA*SET3300	N	Y	HEAT TRANSFER
KPA*TK1000	N	Y	HEAT TRANSFER
KPA*TK5200	N	Y	HEAT TRANSFER
KPA*TK5300	N	Y	HEAT TRANSFER
KPA*TK7000	N	N	PREVENTION
KPA*TK8000	N	Y	HEAT TRANSFER
KPA*TK8500	N	Y	HEAT TRANSFER
KPA*TK9000	N	Y	HEAT TRANSFER
KPA*TK9100	N	Y	HEAT TRANSFER
KPA*TK9500	N	Y	HEAT TRANSFER

Vessel	TBP Present (Normal Condition)	TBP Present (Upset/ Separate Condition)	General Safety Strategy
KPB Unit			
KPB*MIXS1000	Y		HEAT TRANSFER
KPB*MIXS1100	N	Y	HEAT TRANSFER
KPB*TK2000	Y		HEAT TRANSFER
KPB*TK3000	N	Y	HEAT TRANSFER
KPB*TK4000	Y		HEAT TRANSFER
KPB*TK5000	Y		HEAT TRANSFER
KPC Unit			
KPC*CLMN2500	N	N	PREVENTION
KPC*EV2000	N	Y	EVAP COOLING
KPC*EV6000	N	N	PREVENTION
KPC*TK1000	N	N	PREVENTION
KPC*TK1500	N	Y	EVAP COOLING
KPC*TK3000	N	Y	EVAP COOLING
KPC*TK4000	N	N	PREVENTION
KPC*TK4500	N	N	PREVENTION
KPC*TK5000	N	N	PREVENTION
KPC*TK5500	N	N	PREVENTION
KWD Unit			
KWD*TK3010	N	Y	HEAT TRANSFER
KWD*TK3020	N	Y	HEAT TRANSFER
KWD*TK3030	N	Y	HEAT TRANSFER
KWD*TK3040	N	Y	HEAT TRANSFER
KWD*TK4010	N	N	PREVENTION
KWD*TK4015	N	N	PREVENTION
KWD*TK4020	Y		EVAP COOLING
KWD*TK4030	Y		EVAP COOLING
KWD*TK4040	Y		EVAP COOLING
KWD*TK4050	Y		EVAP COOLING
KWS Unit			
KWS*TK4000	Y		HEAT TRANSFER
KWS*TK4000	Y		HEAT TRANSFER
LGF Unit			
LGF*TK1000	N	N	PREVENTION
LGF*TK2000	N	N	PREVENTION
LGF*TK3000	Y		HEAT TRANSFER
LGF*TK4000	N	N	PREVENTION
LGF*TK5000	N	N	PREVENTION
LGF*TK6000	N	N	PREVENTION
LGF*TK7000	N	N	PREVENTION

Table B-2: TBP Prevention Strategy by Vessel

Vessel	Process Feed	TBP Feed Control (P) Prevention or (S) Sampling
KCA Unit Vessels		
KCA*TK1000	KPA*TK7030	P
	KPC*TK4610	P
KCA*TK2000	KPA TK7040	P
	KPC TK4610	
	LGF*DRIP1900	
KCA*FLT7000	KCA*PREC5000	P
	KCA*PREG6000	
	KPC*TK4610	
KCA*FUR8000	KCA*FLT7000	P
KCA*PREC5000	KCA*TK1000	S
	KCA*TK2000	
KCA*PREC6000	KCA*TK1000	S
	KCA*TK2000	
KCD Unit Vessels		
KCD*EV3000	KCD*TK2000	P
	KCD*TK3400	
KCD*TK1000	KWG*DMST1300	P (no Path)
	KCA*FLT7000 from KCA*TK7430	P
	KCA*TK8410	P (no Path)
KCD*TK1500	KA*TK7010/7020/7030	P
	KCD*DRIP1900/3900/7900	P (no Path)
	KCD*DRIP6900/1900	S
	KCD*TK2000 (overflow)	P
	KCD*GB4000 (drain)	P
	KCD*TK4000	P
	KCD*TK4100 (overflow)	P
	KCD*TK7000	P
	KCD*TK7500	P
	KCD*TK3400 (distillate)	P
KCD*TK3210	P	
KCD*TK4000	KCD*EV3000 (Concentrate)	P
KCD*TK4100	KCD*TK4000	P
	KCD*TK3120 (Concentrate)	

Vessel	Process Feed	TBP Feed Control (P) Prevention or (S) Sampling
KCD*TK4200	KCD*TK4100 KCD*TK3400 KCD*TK6000 KCD*TK7000	P
KPA Unit Vessels		
KPA*CLMN6000	KPA*SET3300 KCA*TK1000 KCA*TK2000	P
KPA*CLMN6580	KPA*CLMN6000	P
KPA*TK7000	KPA*TK6010 KPA*TK6510	P
KPC Unit Vessels		
KPC*CLMN2500	KPC*EV6000 (drain) KPC*TK2820 (reflux)	P
KPC*EV6000	KPC*EV2000 (distillate)	P
KPC TK1000	KPC DRIP4900 KWG*CLMN1000 KWG*CLMN2000 KWD*TK4000 KCD*TK7500 KPC*TK9100 KPC*DRIP1900 KDD*TK3500 KPC*CLMN2500 KPC*TK4500 KPC*TK4000 KPC*CLMN2500 KPC*TK5500/5000	P (no Path) P (no Path) P (no Path) P (no Path) P S S P (Pre-TBP) P P P P P
KWD Unit Vessels		
KWD*TK4010	KPB*TK3000	P

Vessel	Process Feed	TBP Feed Control (P) Prevention or (S) Sampling
LGF Unit Vessels		
LGF*TK1000	Lab glove boxes (Aqueous) LGF*TK1700 LGF*DRIP1900 LGF*TK2000 LGF*TK5000 LGF*TK1000	P
LGF*TK4008	Lab glove boxes (Aqueous) LGF*TK5000	P P
LGF*TK5000	LGF*TK4000	P
LGF TK6000	LGF*TK5000 LGF*TK7000	P
LGF*TK7000	LGF*TK6000	P

Source : Shaw Areva MOX Services: Nuclear Safety Evaluation of Facility Explosion Events for MOX Fuel Fabrication, DCS01-AAS-DS-ANS-H-38390-2, page 173 of 518 Section 7.2.7, EXP07.

APPENDIX C

Official Use Only

Response to the Review Comments
by Dr. Dana Powers

On

Risk Assessment of Red Oil Excursions
in the MOX Facility

BNL Draft Report BNL-MOX-2008-001
December 2008

V. Mubayi, BNL
W.A. Mukaddam, CCTI
M.A. Azarm, ISL

February 27, 2009

We thank Dr. Dana Powers (DP) for his review of the BNL report and deeply appreciate the many incisive comments and suggestions he has made. DP has raised a number of interesting, fundamental questions that bring into sharp relief some of the limitations of the BNL study. His exhaustive review of every chapter also throws up some errors of omission and commission in our write-up, which we acknowledge and are glad to correct to the extent possible. Our response to the comments is in two parts. The introductory part deals with the limitations of our study as related to the scope of work we undertook to perform, while the second part responds to each of the detailed chapter comments.

Introductory Response

1. DP raises a fundamental issue: "we don't know what red oil really is" and goes on to comment "that the real cause of red oil events remains unknown..." The red oil event is an explosive event but there is a whole range of explosive events that can occur at various temperatures in the facility. A number of these events, some of which can occur at temperatures much lower than what has hitherto been generally understood as the temperature range for the runaway reaction known as a red oil excursion, have been analyzed by the applicant in the ISA Summary. They include the following: hydrogen explosions, radiolysis induced explosions, hydrogen peroxide explosions, HAN events, solvent explosions, etc. in addition to what the applicant terms and defines as the TBP-Nitrate (Red Oil) explosion. In terms of the conditions under which the red oil excursion has traditionally been defined to take place (e.g. in the Defense Nuclear Facilities Safety Board report as well as by the applicant in the ISA Summary), it occurs mainly at the upper end of the range of temperatures encountered in the facility. We acknowledge that the red oil reaction analyzed in the BNL report is focused on TBP-nitrate thermal reactions. We understand that such reactions occur continuously over a very wide temperature range but the reaction rates are generally low at lower temperatures and the normal heat transfer and venting provided appear adequate. The Tomsk experience, which has been specifically referred to and taken into account by the applicant in the revised red oil strategy, demonstrated that active heat removal processes were already needed at temperatures in the 80 C range; the applicant has tried to provide these through evaporative cooling and adequate venting. Our limited risk assessment was to attempt to erect a simple PRA framework to model: (1) the failure of the evaporative cooling strategy in selected process vessels and (2) the failure of the TBP prevention strategy, through formation of emulsions, third phase, rag layer, etc. The latter failures of course overwhelm evaporative cooling but they involve multiple failures of controls. In effect, what DP appears to be asking for is a more complete risk assessment to model the impact of many uncertainties in the process chemistry on the red oil phenomenon. Our charter was more limited.
- ~~2.~~
2. DP raises another basic issue: the importance of radiolytic processes as contributing not only to the heat up of vessel contents but, more importantly, to the formation of reactive chemical species. He indicates that "hydrocarbon radiolysis has not received the attention that has been devoted to water radiolysis." We acknowledge that our study was very limited in that respect. The applicant looked at radiolysis caused explosions in the ISA Summary but that analysis was limited to water radiolysis only, i.e., the generation of hydrogen and explosive H₂ concentrations in various AP processes, and a listing of the various controls designed to limit or control H₂ generation. A larger study including the radiolysis of hydrocarbons and its possible impact on the creation of reactive

chemical species would have involved a much larger effort than what was possible under the task assigned.

- The interest in the study expressed by DP as revealed by his comments and the guidance offered to BNL by the NRC (particularly NMSS reviewers) were different. DP appears to look at this study as erecting a basic framework that can then be employed to do more detailed work on the numerous uncertainties that surround the issue of red oil in the context of assessing the viability of the strategies employed to deal with it by the MOX facility, e.g., the impact of radiolytic processes on the formation of reactive species that can then influence red oil decomposition, etc. The guidance from the NRC, on the other hand, was directed more at helping staff to resolve issues pertaining to the prevention of red oil excursions in a risk-informed manner based on the applicant's design, i.e. is the facility safe enough as far as red oil is concerned? Our study was directed more at the latter definition of the issue. We accepted broadly the characterization of the red oil phenomenon developed by the applicant and then tried to assess, within a probabilistic framework, to what extent the strategies offered by the applicant were successful in meeting the challenge. DP would probably have us do something different, which is extremely interesting and challenging in its own right but will take additional time and effort.*

Detailed Response to Comments

- The authors have taken on a formidable task with limited resources in time if nothing else. In this regard they have assembled a formidable amount of material and applied a wealth of thought to the issue of 'red oil' events in the processing of fuel. Certainly, they have clarified positions in a proposed process stream where red oil events can take place. Most importantly, despite great uncertainties in probabilities, they have used a method that identifies the most critical safety systems employed in the process to prevent or mitigate red oil events. The application of risk methods to reprocessing technology is pioneering. This aspect of the work deserves more emphasis in the document and is certainly the greatest strength of the work. There is much that can be built upon in this first effort to apply risk methods. Criticisms presented below ought not take away from what is a monumental effort that does much to contribute to the safety assessment of mixed oxide processing facilities.

We fully appreciate DP's deep understanding of the PRA concept and the challenges we faced in conducting the first of a kind PRA for fuel process facilities with very limited data and experience as well as uncertainty in the knowledge of the processes being analyzed. We do agree this is just the start of a technical discipline that has much room to grow.

- A central issue that permeates the entire effort is that we do not know what red oil really is. The authors seem to be aware of this when, on page 3-7 and continuing to page 3-8, they note the effects of irradiation and the low temperature onset of the Tomsk event. Still much of the report follows the application contention that the red oil event is the result of strictly thermal reactions between tributyl phosphate and nitric acid. To be sure, tributyl phosphate and concentrated nitric acid can form adducts that decompose exothermically. It is not apparent that these adducts are indeed the cause of the dramatic, explosive events that have occurred in fuel process facilities. Indeed, there is a substantial body of opinion that radiolytic decomposition of tributyl phosphate, perhaps

also involving the organic solvent lead to the product that decomposes so explosively. Most events in the past have taken place in locations where an accumulation of radiolytic products could be expected. In this regard, the authors may want to include radiation dose rates among the variables such as temperature, concentration and residence time that they use to screen processes for susceptibility to red oil phenomena - both formation and decomposition. I think the document needs to emphasize that the real cause of red oil events remains unknown and that this mandates a significant attention to safety margins and perhaps defense in depth. This uncertainty in cause contrasts sharply with issue of criticality events where causes are well understood and targeted strategies and double contingency principles have worked well to prevent events from occurring.

Comments on most of this have been provided in the introductory response, however, as suggested by DP, we will include radiation dose explicitly as another variable that can affect red oil excursions.

3. Consequences of the possibility that alternative scenarios for production of explosive byproducts need to be considered. One comforting feature of the proposed system is that dose rates are not expected to be especially high since the decay rates of radionuclides involved in the process are not especially high. It appears that the applicant is taking steps to avoid accumulation of byproduct species. The question becomes, then, is these steps adequate?

Not only are the decay rates of the radionuclides fairly low, the quantities involved in the MOX facility are also quite small. In the acid recovery system's first stage evaporator, the concentration of Pu and U is in the range of 15 mg/L, and it is approximately the same in the concentrates tank. While the concentration of Am is significantly higher in both vessels at around 3 g/L, this is still at least an order of magnitude lower than the radionuclide concentration at which alpha radiolysis studies have been done in the past (e.g., the ORNL report "Alpha Radiolysis and Other Factors Affecting Hydrolysis of Tributyl Phosphate, ORNL/TM-9565, June 1985). However, more work may need to be done to adequately treat the issue of radiolytic dissociation of organic compounds.

4. The authors have undertaken an assessment of risk which they define as the product of event probabilities and event consequences. The authors are challenged by the definition of consequences of red oil events. There is not a clear definition of the consequences of interest. The proposed facility located as it is on a large government reservation is isolated from what would be generally recognized as "the public". This isolation is neutralized some by the regulatory classification of employees at the Savannah River Site but not associated with the process facility as members of the public. Still, it is not evident that an explosive release would distribute enough radioactive material to constitute an unmanageable threat even to this population of the co-located workforce. It appears, then, to be the threat to the workforce associated with the facility that is the main consequence of interest. This has always been a challenge for analysis since those most at threat may or may not be positioned sufficiently close to the site of an explosive event to suffer any consequences from radiation release. Within the chemical process industry it has become common to use societal measures of event consequences rather than individual consequence measures because of the uncertainties in employee locations at the time of events. That is, the individual consequences delineated on page 2-2 might be better replaced with societal expectation

values. Even with the individual dose criteria for consequences, it is not clear that all red oil events are equal in the various locations identified in the document.

The applicant assumes that the consequence of a red oil excursion, radiological or chemical, is "High" for the facility worker. Hence, by the performance criteria of Part 70.61 the likelihood of a red oil event has to be made Highly Unlikely. The same approach has been adopted in this study; with the information available, it would have been impractical to evaluate radiological doses or chemical exposures to facility workers in the proximity of various process equipment cells where a red oil event could conceivably occur.

5. Certainly, it would seem likely that inventories of radionuclides available for dispersal by an explosive event would differ significantly. No account is made of the potential consequences associated with the scenarios suggested in the document. With these introductory comments, it is possible to proceed to the details on the document. The first chapter is introductory in nature and presumes some general familiarity with the history of red oil events. The second chapter discusses the safety strategy developed by the NRC regulatory process. It probably is not useful to comment on either of these chapters except to say they provide an adequate introduction to the rest of the document.

Chapter 3: The Red Oil Phenomenon

6. It might be useful in Section 3.1 to note that the materials involved in the Tomsk event had somewhat different chemistry than the process chemistry that has been used in the USA and the process chemistry that is proposed for the MOX facility.

We will try to include, as suggested, some additional references to the Tomsk event.

7. A reference is needed for the nitric acid/water azeotrope in section 3.2.

This will be provided.

8. The diagram in figure 3-1 specifically neglects radiation dose as a contributor to the formation of red oil. I think this can be misleading. One misleading comment arises immediately following where it is asserted that contact between the solvent or diluent, in this case hydrogenated propylene tetramer, cannot lead to the formation of explosive compounds. This may be true for an idealized system, but radiolytic processes can intrude. Hydrocarbon radiolysis has not received the attention that has been devoted to water radiolysis. Hydrocarbons can still undergo reactions including the formation of unsaturated and even oxygenated species. There does not appear to be abundant data for the diluent to be used here, there are data for diluents used in the past. Most troublesome is the radiolytic formation of alkenes that can subsequently react with radiolytic species such as ozone or peroxide.

Radiation dose will be mentioned and briefly discussed in the revised report. As noted in the Introduction, the analysis of the formation of chemical species by radiolysis of hydrocarbons will greatly enlarge the scope and level of effort necessitating a significant amount of additional work.

9. I do not understand the dependencies listed at the bottom of page 3-2. It appears to me that knowing the rate of formation and the length of exposure is enough to know the amount of red oil that has formed. The total material does not seem to be material unless the rate of formation is meant in some sort of rate per unit volume or per unit surface area. It might be noted that the rate of formation need not be constant. There may be some induction period before reactions can take place that lead to red oil formation. I think the authors know what they mean here, but they need to be a little more disciplined in their language.

The write-up will be checked and more disciplined language will be used.

10. The report quotes the Defense Nuclear Facility Safety Board in noting that temperatures below 130°C are often quoted as sufficient to protect against the explosive decomposition of red oil. It is not evident how well founded this statement is nor is it immediately clear that Tomsk does not stand as a clear counterpoint to this assertion.

A clarification will be added in the revision.

11. Equation 1 is offered as a rate expression. No source is associated with this rate expression and the document does not provide any substantiation for the rate expression. (I do note that the agency generally prefers SI units for this sort of an expression rather than using 1.9872 cal per mole-K as the value of the gas constant! The document uses a variety of unit systems at various locations. Though this does not really detract from the reading, it is not a good practice.). The rate expression is remarkable in that there is no dependence on the organic phase concentration or contact area. Apparently, the reaction to form red oil is believed to be a homogenous process.

Equation 1 will be clarified and converted to SI units.

12. On pages 3-3 and 3-4 some decomposition reactions are cited. No radiolytic reactions are cited and butanol is susceptible to radiolytic decomposition in a variety of ways. The assumption being made here is that the red oil phenomenon is associated with a thermal formation and decomposition of some simple adduct. This is not known. One can readily imagine that radiolytic process lead to the formation and accumulation of species such as organic peroxide or ozonides. Such species are known and are known to decompose explosive by free radical chain reactions. Formation of such species is not inconsistent with the empirical observation that red oil events appear associated with long term exposure to heavily irradiated mixtures of organic and concentrated nitric acid. Decomposition of such species could be accelerated under suitable conditions such that neither venting nor evaporative cooling could respond sufficiently to prevent damage and perhaps dispersal.

As stated before, radiolytic dissociation of organics to form new reactive species was not studied in the BNL report. It will require significant additional time and effort.

13. There is a change of nomenclature that is probably just typographic in equation (2) where $(C_4H_9)_3PO_4$ appears rather than the more familiar $(C_4H_9O)_3PO$.

This will be corrected.

14. On page 3-5 there is a reference needed for the heat of vaporization of butanol.

This will be provided.

15. I have absolutely no idea what the rate constant attributed to Paddelford and Fauske really is. On the face of the words in the text, the rate expression would be a 15.4th order reaction! I think that one needs to write the rate expression here rather than just the rate "constant" since reaction (2) is obviously not elementary. Even with the rate expression, because the reaction is not elementary, there are some very tight constraints on where the rate expression would be applicable.

This will be clarified and re-stated to remove the ambiguity in the current write-up.

16. Page 3-6 states that the amount of organics is expected to be low because solubilities in weak acid are low. This certainly is not true of either butanol or butylnitrate as shown on early pages in connection with the decomposition of tributyl phosphate. Both these organics have very high solubilities in water. It also seems to discount the possibility of emulsions forming the entrain micelles of organic in water or water in organic. Emulsions can be amazingly stable and can provide a means to avoid segregation of organic and aqueous phases. Radiolytic processes can lead to substitutions on long chain hydrocarbons that are conducive to the formation of emulsions.

The organics here refer to TBP and the solubility of TBP in weak acid is low. This will be clarified. Emulsion formation is explicitly discussed and is analyzed later as a phenomenon that can potentially defeat the preventive strategy of the applicant. However, the possible impact of radiolytic processes on emulsion formation has not been discussed.

17. On page 3-6, a reference is needed for the comment "...as reported elsewhere..". The entire discussion is a bit confusing since gases do not really enter into any of the reactions discussed to this point except as products. Increasing their concentration in the liquid by pressurization is not going to speed up the reaction rate. The "...kinetic features of the thermochemical degradation..." is not a readily interpreted statement. I think the authors simply mean a thermal degradation and that they discount any catalytic processes or chain reaction processes being involved for reasons that are not stated. At the bottom of the page is a tortured discussion of the possibility of thermal runaway that is not entirely accurate. If the rate at which the reaction accelerates with increases in temperature exceed the rate at which heat losses increase with increases in temperature, one will get runaway.

The discussion on p. 3-6 is about vent size and the so-called Fauske criterion. Back pressure will increase temperature and consequently the reaction rate for a certain vessel volume. Perhaps the discussion of the thermal runaway from the results of the paper by Nazin et al is a bit tortured and can be simplified as suggested by DP.

18. A significant error is perpetuated by table 3-1 and the surrounding discussion. The red oil decomposition reaction is an exothermic reaction. There is no "onset temperature" for the reaction. It occurs at all temperatures. The rate may be too slow to detect at low temperatures, but the reaction is still occurring. Any onset temperature is dependent on the ability to remove heat from the system caused by the reaction. One could easily

design configurations of limited heat loss and see "onset" of the exothermic reaction at almost any temperature where liquids still exist.

Table 3-1 is reproduced verbatim from the Nazin paper; the word "onset" is simply analogous to a point of inflection on the pressure and temperature time history curves; maybe a more suitable word can be used to clarify it. There is no intent to suggest that the reaction does not occur at lower temperatures.

19. At the conclusion of page 3-7, the authors acknowledge radiation may play a role but they do so in a way that seems to suggest that only the heating from radiation is important. They do not seem to want to consider that reactions of radiolytically produced species leads to red oil formation.

DP is right to remark that reactions of radiolytically produced species were not considered, it will take significant additional resources and time.

20. A reference is needed for the work of Tashiro cited on page 3-8.

This reference was provided in a report that the authors could only see in AREVA's offices in Bethesda but not copy. We will ask NRC to help us retrieve it.

21. Reference 3-3 is incomplete in the list of references.

This will be provided.

Chapter 4: Red Oil Safety strategy in the CAR and the License Application

22. This chapter is more a recitation of the license contentions. I provide some limited comments. First among these is that simply assuring that the rate of heat loss exceeds the rate of heat generation is not sufficient to provide safety. One needs to assure that the increase in the rate of heat generation with an increase in temperature does not exceed the increase in heat loss rate with temperature. To do otherwise risks fluctuations in rates leading to runaway reactions.

The strategy appears to be based on the idea that adducts formed by thermal reactions of tributyl phosphate with nitric acid are the cause of red oil events. The reaction process to be dealt with then is simply a thermal decomposition. There is no proof that this is the case for the process considered here or for the events that have taken place in the past. For example, peroxides and the like could be responsible. The reactions of these species can progress autocatalytically and there will simply be no time for evaporative cooling to quench the reaction. Would evaporative cooling work if TNT were floating through the system? The applicant is defining a benign process for formation and decomposition and then arguing that a benign mitigative strategy will suffice without ever showing that the reactants are in fact the hazardous species.

Much of the available literature does seem to suggest that red oil phenomenon is a thermal decomposition; maybe there is no proof that this is solely what happened in past events but by the same token it is also problematic to argue that peroxides could be responsible. The argument made by DP in this and subsequent paragraphs seems to

suggest that neither prevention nor mitigation via evaporative cooling can be demonstrated to work since there is a great deal of uncertainty about the chemistry of the process. We agree that there probably is a fair amount of uncertainty in the process chemistry but our scope of work was limited.

23. The challenge raised by the revised approach based on prevention is that it relies heavily on compliance with administrative controls (Enhanced Administrative Controls as discussed on page 4-5). Violation of the controls are errors of commission and these are quite difficult to analyze in a risk framework. This poses a challenge to the analysis proposed in this document that really is never addressed. Errors are treated within a context of omission and not commission.

While administrative controls are one element of the control strategy, there are numerous active engineered controls also, so it is perhaps an overstatement to say that prevention relies "heavily" on administrative controls.

24. A mystery emerges in the design of controls. Arguments made within Chapter 3 show that carryover of organic with the aqueous phase is to be minimized. Emulsions are a mechanism for carryover, but there appears to be no steps taken to assure emulsification does not occur.

The numerous pulsed extraction columns in some process units, in particular the purification unit where the first extraction process takes place, are a means of reducing the likelihood of stable emulsions being formed in the extraction process or of breaking up emulsions if they do form. However, emulsification as an initiator of red oil has been analyzed in the report.

25. Venting sizes adopted by the licensee may be widely used, but they do not assure red oil explosions will not occur. We only know that when adequate vents have been used along with any number of other measures to avoid red oil events, we haven't had any events. All we really know is that smaller vents available where red oil events have taken place were not adequate.

The report points out that there is uncertainty regarding vent sizes available in the context of the red oil excursion.

26. I can find no basis for the confidence that the amount of TBP carried over to the KPC unit is limited to 50 grams per liter (page 4-10). This limit seems to be based on solubility and neglects both entrainment and emulsification.

This amount of carryover based on solubility is during normal operation; the report analyzes scenarios where entrainment, emulsification, and formation of a third phase could cause this limit to be grossly exceeded. Incidentally, during the site visit the BNL team was informed by the applicant that 30 years of French experience have demonstrated that the amount of carryover in normal operation is around 20 gm/l; but since this information was anecdotal it has not been used in our assessment.

27. I should not think that a flash point check is adequate to show the diluent is not accumulating radiolytic decomposition products that would influence red oil formation. For example, alkene formation followed by epoxy formation and decomposition to

produce long-chain hydrocarbons could produce surface active agents that influence emulsification.

As noted earlier, we did not look at radiolytic decomposition.

Chapter 5: MOX Facility Operations Risk Ranking

28. This portion of the study looks at risks of red oil events in process streams. It specifically excludes initiations caused by fire heating solutions over administrative limits or seismic events mixing solutions that ought to be kept separated. That is, only process events that occur despite the precautions are to be considered. This seems a reasonable restriction of scope to take given that this is but one element of a larger effort to assess the safety of the proposed process facility.

We agree that global initiators such as internal fires, external hazards like seismic events, and loss of power/station blackout events need to be evaluated, however, the scope of the effort was limited in that respect.

29. A more bothersome aspect of the study is that it neglects shutdown events in which there is a failure to purge the process lines. This has been a remarkably common event in many Department of Energy facilities. Protracted shutdowns are mandated because of changes in policy or some misadventure with in the Department of Energy. For the MOX facility shutdown could occur because of interruptions in the supply of feed. When there has been shutdown and improper layup of a facility (commonly none at all!), the recovery often does not go smoothly. Especially with radioactive feeds stored in the lines, strange and often obnoxious chemical species begin to form and accumulate. Temporary shutdowns that can go on for months may pose hazards that are not obvious from the flow sheets of a process stream.

We agree on the importance of looking at process shutdowns and subsequent start-ups. The impact of the failure of the six-monthly flush out of some process vessels on red oil excursions was evaluated but a global study of potential shutdown failures was not carried out due to resource limitations.

30. For the analysis, eight units are considered:

KPA - purification cycle unit
KPB - solvent recovery unit
KCA - Oxalic Precipitation and Oxidation Unit
KCD - Oxalic Mother Liquor Recovery Unit
KPC - Acid Recovery Unit
KWD - Aqueous Waste Reception
KWS - Solvent Waste Reception
LGF - Laboratory Liquid Waste Receipt

31. Figures 5-1 and 5-2 are essentially unreadable. Much of this chapter is simple description of the process and does not call for much in the nature of comment. I do comment that:
- evidence that tributyl phosphate solubility in nitric acid is not susceptible to either "salting out" or "salting in" is not provided. Without this information solubilities

listed in Table 5-1 cannot be considered applicable to the process stream in question.

- the description of the processes notes formation of what is termed a "rag" layer which is apparently an emulsification region between two contaminated phases.
- there seems to a confusion between red oil formation and red oil decomposition.

Red oil formation may not require elevated temperatures. Red oil decomposition that could produce accidents may require temperatures above ambient. I know of nothing in the literature that demonstrates elevated temperatures are required for formation of energetic reactants. Certainly elevated temperatures are not required if the energetic materials are the products of radiolytic reactions. Consequently, I think it incorrect when it says on page 5-5 in connection with PULS 2000 that "Because of the relatively low temperature (ambient), the rate of red oil formation is expected to be very low."

The Figures were reproduced from the License Application and do not appear to have reproduced well. We will try to have better copies made. We will take another look at available data to see if there is information on "salting in" or "salting out". We thank DP for alerting us to the possible confusion between red oil formation and decomposition and will clarify the write-up.

32. The process descriptions in chapter 5 are punctuated by episodic judgments offered by the authors on the likelihood of red oil formation and red oil decomposition (Again, there may be some confusion between formation and decomposition.) These judgments are based on temperature, residence time and concentrations. There is no mention of dose as a possible, essential, factor in the formation of red oil. Again, the authors have adopted the view of the application that red oil formation is a strictly thermal process and it is not evident that this is a defensible position. In any case, it would make the document much more readily understood if the segments in which the authors offer their judgment about the susceptibility of the elements of the flow stream to red oil formation and decomposition were separated and highlighted.

It is true, as indicated earlier, that we did not consider the impact of radiolysis on red oil formation and decomposition.

33. On page 5-5 three terms are introduced that are not self defined: "inadequate coalescence," "flooding," and "formation of a third phase." I believe the authors eventually discuss these - page 5-29. They need to provide the reader some assurance that the terms will be defined and may want to consider introducing these terms earlier in perhaps Chapter 4.

These terms will be defined before they are mentioned.

34. On page 5-6 the authors assume as does the applicant that red oil is formed by reaction with tributyl phosphate or one of its decomposition products. The hydrocarbon diluent is not involved. Certainly, one would not expect the hydrocarbon to be involved if one were confident that red oil formation is a thermal process. The possibility that red oil is the product of reactions with radiolysis products brings the hydrocarbon back into consideration. One can readily imagine radiolytic formation of alkenes and reaction of ozone or peroxide from solution to form organic ozonides or peroxides that are susceptible to explosive decomposition.

See attachment for the response.

35. Mention is made of quality of hydrocarbon quality. The measurement of bromine number is undertaken, on presumes, to detect the formation of alkenes probably by radiolytic processes. The concern is that reactive species can add across double bonds - notably ozone and peroxide produced in water radiolysis can add across double bonds to produce species that undergo complex and often energetic reactions. See for example the complex mechanisms associated with Criegee intermediates in the ozonation of oleic acid. Why is it assured that analogous species do not contribute to the Red Oil problem?

See attachment for the response.

36. On page 5-7 the question arises on whether aluminum nitrate will cause tributyl phosphate to salt out of solution or salt in. Whereas usually electrolytes cause salting out of nonelectrolytes, it is not unheard of for some salts to cause salting in. Borates for example can cause salting in of nonelectrolytes in aqueous solution.

We did not consider this possibility.

37. Page 5-10 includes a mention of intermittent feeds causing mixing of light and heavy phases. This leads to the possibility of carryover. Is this possibility included in the risk analysis? Is the probability susceptible to quantitative analysis? Table 5-1 is a bit of a mystery to me. The solubility of TBP in water is not so much the issue as is the partitioning of TBP from the organic phase to the aqueous phase. Why are not solubilities and partitioning of DBP and MBP of equal interest and also merit tables in the report? Incomplete draining is mentioned on page 5-14, but it is not clear to me how this was recognized in the risk assessment. It is argued on page 5-15 that the aggressive conditions in EV 6000 assure the rate of destruction of TBP is greater than the possible rate of accumulation. The risk of Red Oil, it is argued, is mitigated. But, if the reactions of the products of TBP decomposition with nitric acid are responsible for Red Oil, is the argument misplaced?

The possibility of carryover is included in the risk analysis. Chapter 6 provides a discussion of the probabilities that were assigned. Table 5.1 was generated from a combination of two sets of data: (1) the solubility of TBP in water and (2) a correction for the solubility of TBP in various acid concentrations. Note that this is in the absence of an organic phase in contact with the aqueous phase. If then one adds an organic solvent, e.g. a TBP/HPT mixture with 30% TBP, a portion of the TBP would be extracted from the acid phase to the organic phase if the partition coefficient of TBP favors the organic phase. That is indeed the case.

From the data that were readily available to us, the TBP partition coefficient defined as: [weight concentration of TBP in the organic phase/weight concentration of TBP in the aqueous phase] is greater than 10. For example, in 2M HNO₃ at 20^o C in contact with TBP + Hyfrane (trade name for HPT) mixture, the partition coefficients ranged from 10 to 100 (Germain, M. and Pluot, P., Proc. Inst. Solvent Extraction Conf., 1980, Vol. 3, Leige, Belgium, 1980, pp 80-218, cited in Science and Technology of TBP, op. cit. Ref. 5-4 in the draft BNL report). Thus, in effect, the solubilities shown in Table 5.1 appear to be the bounding condition for the amount of TBP in the aqueous phase.

We should mention that we do not have partition coefficient data for a range of HNO_3 concentrations. We have assumed from our reading on the subject that it would not be less than 1.0. The applicant may have actual data for the conditions used in the process.

The source of DBP and MBP in the aqueous phase depends on their concentration in the organic phase. For two reasons, we believe that to assume that all organic species are TBP is a reasonable assumption. (1) TBP is a fairly stable compound (thus its extensive use in extraction of metals from nitric and phosphoric acids); the rate of its hydrolysis is slow and the extent of hydrolysis is not significant under most operating conditions. However, despite the slow rate of hydrolysis, DBP and MBP would accumulate in the solvent phase if it were not continuously removed. The process has a solvent treatment section where the organic phase is continuously treated to remove these degradation products. The accumulation of these compounds is monitored due to its deleterious effect on the extraction performance. (2) We believe (although we need to check this further) that the energy release from TBP decomposition is greater than that from its degradation products.

The risk of red oil excursions in EV 6000 is treated in more detail in Chapter 6.

38. The significance of the equation on page 5-18 is not immediately apparent. It appears to only serve to define the meaning of a heat transfer coefficient. It certainly does not elucidate the relative importances of steam side and porous side heat transfer coefficients which seems to be the point in the text. Some sort of serial heat transfer rate would better serve the purposes of the text.

This will be clarified in the rewrite.

39. The mention of "...numerous recoded incidences ... on page 5-19 needs a reference. Also on page 5-19, it is not clear how uncertainty in the draw off from the evaporator has figured in the assessment of risk.

The reference will be supplied.

40. On page 5-20, the catalysis by manganese ions needs a reference.

This is taken from the applicant's process description in the License Application (see page 11.2.11-4).

41. The slab settler (page 5-24) does not assure that the aqueous phase is organic free if TBP and its decomposition products can partition from the light organic phase to the heavier aqueous phase.

The objective of the slab settler is to minimize the presence of non-soluble TBP in the aqueous phase. The possibility of its failing to do so and the extent of the failure is analyzed in the risk assessment in Chap 6.

42. Also on page 5-24, the assertion that a red oil event is "inevitable" in the evaporator if sufficient organic material is present seems a bit strong.

A suitable word change will be made in the rewrite.

43. Figure 5-8 is essentially unreadable. If you puzzle out the figure, it really does not help to understand the equation. Terms need to be better defined in the equation. Table 5-2 is a mystery. What are the cases being examined here?

The figure will be made clearer and the equation will be clarified. Table 5-2 shows the range of densities of the aqueous and organic phases in relation to the height of the interface over which the slab settler will continue to work, i.e., the seals will remain intact as long as the densities remain in the range considered. The analysis is limited as it is a static head analysis, which assumes equilibrium is reached to allow the phases to separate. However, emulsification, rag layer formation, etc. will tend to defeat the normal operation of the settler and these possibilities are examined in Chap 6.

44. The use of hydrogenated propylene tetramer rather than the usual normal paraffinic hydrocarbon is lauded on page 5-28, but I have no information on the enhanced stability of this tetramer especially in a radiation field.

We do not have information or data on the stability of HPT under radiation. However, as far as chemical stability is concerned, no double bond and pure components make HPT much more stable compared, for example, to kerosene.

45. Also, on page 5-28, the authors bring up the important point of degradation and fouling of equipment in the process units. These are very difficult things to include in a risk assessment. They make the probabilities time dependent. How did the authors tackle this headache that is usually neglected in risk analyses for power reactors?

This is a very important issue and we are very glad that DP has mentioned it. We recognize that fundamental improvements to conventional PRA methods are needed in several areas, like, for example, in the treatment of time dependent failures. A proposal to this effect was submitted by BNL to NRC over two years ago as part of methodological improvements needed in the PRA of nuclear-chemical facilities when the first study of red oil excursions in the CAR design of the MOX facility was conducted.

46. I am surprised that incomplete draining mentioned at several points in the text is not included in the list of conditions on page 5-29.

We thank DP for drawing our attention to this. It will be included in the rewrite of the report.

47. Under item 4 on page 5-29, the term "high steam coefficients" is used. The meaning is not clear. I suspect that the authors mean the high convective heat transfer coefficients on the steam side. They should make the terminology clear.

It will be clarified in the rewrite.

Chapter 6: Red Oil Safety Strategy - An Overview

48. Chapter 6 begins with a description of the applicants proposed safety strategy predicted as it is on the belief that red oil formation is a thermal process and that the decomposition rate is neither autocatalytic nor a chain reaction. There does appear to be

some confusion in the text between red oil formation and the decomposition of the red oil. I have not flagged every point where there appears to be this confusion. The authors may want to re-examine the text to assure that the reader does not become confused by the separate issues of red oil formation and decomposition.

The text will be re-examined to make sure that red oil decomposition and formation are not used interchangeably. We think the question mostly applies to the wording used in describing the heat transfer strategy, where the process described is mainly a steady state thermal balance at a fairly low temperature (close to ambient temperature).

49. The "semi-empirical model" mentioned on page 6-2 is not further referenced. What is it? Is it the same as the semi-empirical model mentioned on page 6-7 and otherwise not further described? This model appears to be based on a hypothesis concerning the nature of red oil that has not been validated. All we really know is that the model applies to a species in the system that can be decomposed exothermically. We do not know that this energetic species is what was responsible for the red oil accidents at fuel reprocessing facilities.

The semi empirical model in page 6-2 is the same as the one in page 6-7. It is referenced in a descriptive and qualitative manner in the applicant's ISA Summary. Our own limited understanding of what this model is is with regard to the success criteria for evaporative cooling mentioned on page 6-7 and referenced in Ref. 3-12 in Chapter 3. DP's point regarding the uncertain and varied nature of the red oil reaction is well taken. We have focused on the traditional definition of the red oil excursion due to a runaway reaction of TBP with nitric acid. As pointed out earlier, we did not undertake any systematic assessment of the radiolytic dissociation processes that could be involved as well as some other chemical degradation mechanisms, perhaps wrongly so, because of the following assumptions:

- *The dose rates involved in this facility are expected to be much lower than other facilities where exothermic explosive events attributed to red oil have been observed at a lower temperature.*
- *The regular flushing of the vessels, sampling/analyzing, and use of fresh diluents.*
- *The catalytic effect of plutonium, uranium, and zirconium was considered in the semi-empirical model constructed by the applicant.*

Some of these issues were discussed verbally and albeit informally with the applicant during the first and only site visit back in early June of 2008; however any independent assessment was considered far beyond the scope of the PRA.

50. It is not clear when in the system situations arise in which there is TBP phase but no hydrocarbon solvent. It is then not clear when the four conditions listed on page 6-7 are applicable.

The conditions are applicable for cases where either no HTP or only a very little amount of HTP is expected. These conditions are mainly used for analyzing the evaporative cooling strategy for vessels such as evaporators. Note that as stated in page -8, "IROFS density controls in the KPC buffer tank therefore would detect HTP and prevent HTP from passing downstream...". So, under normal conditions, we do not expect HTP be present in any significant amount. Under a severe upset condition, the PRA does not

really credit evaporative cooling and the sequences usually contain only the failure of prevention strategy and the occurrence of the initiator.

51. Why is not failure to flush systems every 6 months not included in the list on page 6-8?

DP is correct, it should be included. It is a necessary condition for evaporative cooling to work. We will explicitly add it in the final report.

52. On page 6-10 there is a discussion of the applicants plans to flush the KPC every 6 months. The technical basis of the time interval for flushing is unclear to me and is not discussed in the document. One would have expected the schedule for flushing would be augmented by some positive indicator of the need for more frequent flushing especially since different types of feeds will be used in the proposed system. There are, then, two possible scenarios:

- flash does not occur per the schedule
- the schedule for flushing the system is inadequate and flush is needed prior to the schedule.

It appears that the authors have only considered the first of these possible scenarios.

The six month time interval is based on limiting the normal accumulation of TBP in any vessel in KPC below 21 liter as stated in page 6-10, "This strategy is based on the maximum calculated accumulation rate of separate phase TBP, which indicates that at most 21 liters of TBP..."

Adequacy of the flushing system is a difficult question since it is not clear what attributes have to be met to declare the process adequate. For limiting the total amount of TBP the flush would be adequate under nominal parameters, and if deviations from nominal operation occur it would be taken into account. However, if the adequacy refers to preventing accumulation of degraded chemicals due to radiolytic, chemical, and thermal processes; this would depend on the sampling, what is being analyzed, and what are the limits that require actions. The latter has not been investigated by this study. Therefore, the question of inadequacy from the latter aspect has not been raised in the current PRA.

53. At this point the authors begin what is the most significant part of the work. They utilize event and fault tree methodologies to estimate risk. They are plagued by the lack of data for event probabilities and they forced to make estimates with fairly broad error bounds (They might want to remind readers what is meant by error factor in connection with a lognormal probability distribution since it is not broadly common nomenclature.) But, a far more important part of the effort is that they identify dominant cut sets. This allows them to draw attention to the crucial safety systems among all the systems applied to prevent or mitigate red oil events. This, I should think, would be the most useful result for the NRC staff to come from this work. True enough that the dominant cut set may be affected by the assumed probabilities **and the entire analysis is predicated on accepting the applicants' hypothesis of the real threat.** Still, the ability to know for each system what is crucial is the first step to the design of a rational defense in depth strategy that might compensate for unknowns and uncertainties. I should think this aspect of the work deserves to be far better highlighted in both the executive summary

and in Chapter 7 rather than the qualitative or quantitative estimates of the likelihood of a red oil event.

The authors fully agree with the comments and Chapter 7 as well as the executive summary will be modified to highlight DP's comments.

54. Chapter 6 is the real heart of the contribution made by the authors to understanding the safety of the proposed process facility. It is unfortunate that many of the event trees (see for example 6-1, 6-2, 6-3, and 6-4) cannot be read by the tired eyes of this reviewer.

BNL will attempt to enlarge the event tree graphs to make them more readable as a part of the report update.

55. It is in chapter 6 that it becomes apparent that the authors are aware very much of the problems caused by the formation of emulsions. There is not, however, any attempt to define conditions that are conducive to emulsion formation that may be undetectable to the proposed instrumentation and administrative controls. Can one identify process conditions that lead to emulsion formation and should be avoided?

Prevention of emulsification and understanding its contributing causes is an important engineering and design issue which is worth examining in more detail. In the PRA we focused on the occurrence of emulsion in an extraction column causing TBP carry over as an initiator. We also focused on the means to detect inadvertent transfer due to emulsions and limit the amount by nominal flow rates. The general question of emulsion prevention was considered outside PRA scope.

56. On page 6-13, the authors justify the use of one failure a year based on having used this value before. This really is a weak justification. What one would like to know in the absence of data or a justified failure rate is whether there is a critical failure rate that leads to unacceptable risks.

The one per year frequency was the result of an ad hoc telephone survey of some chemical processing plants that also use liquid-liquid extraction technology. It can be used for base case analysis. We can then determine what should be the critical failure rate that leads to an unacceptable risk via sensitivity analysis. This can be highlighted in the report.

57. At some points in chapter 5 and 6 the authors note formation of a third phase – perhaps a micellar phase dispersed in the liquid. It does not seem to be pursued or further explained. For example, one can imagine that radiolytic processes lead to formation of long chain organic alcohols or carboxylic acids that are surface active and can stabilize globules of solvent containing tributyl phosphate within the aqueous phase. Formation of emulsifying agents may not be necessary. It is evident that at points in the process we have small density differences and well mixed conditions. These are necessary conditions for simple entrainment of the organic phase into the aqueous phase.

There are two different phenomena that may lead to what is generally referred to as the third phase. The first phenomenon is the result of forming a complex that has a high density or a peculiar phase diagram. In the MFFF, the applicant has added appropriate chemical agents to control the well known third phase formation due to an extractant rich in heavy metals (e.g. the TBP/Pu^{IV} complex which is nearly insoluble in HTP). The

complex may also have a peculiar phase diagram, such that it is below the heavy phase (because of density) and does not get a chance to get into the lighter phase even though the partition coefficient may favor it belonging to the organic phase, or it is not soluble in either phase and thus forms a third phase, which may lie below, in between or above the two phases depending on its density.

The other phenomenon is emulsion formation. This is what DP seems to refer to. Degradation products or some other surface active agents (usually ionic agents or long chain soap-like compounds, amphiphile) may cause micellular formations like soap does. This phenomenon does not require a large concentration of the agent causing this to occur. This is what we refer to as emulsion in the report and it can exist as a third phase between the heavy and light phase.

A potential third phase due to radiolytic processes has not been discussed. Again, we feel this is beyond the scope of this early pilot PRA.

58. I do not find a basis for the assertion that the probability of loss of temperature control is $2.2 \times 10^{-3}/\text{yr}$. The estimate intimates that there will be no loss of temperature control over the lifetime of the facility, which may be true. It does need some justification since loss of temperature control is not uncommon in process facilities. Usually sensors get corroded.

The temperature control for the Hot Water System consists of two independent trains in hot water environment. It was estimated through fault tree analysis and generic data. However, the authors have been concerned in some cases about the effect of the harsh chemical environment on some of the equipment failure rates. To the extent possible we have tried to use the limited data from the Savannah River site, hoping that some of these considerations are reflected in the estimated failure rates. An international data collection and estimation is one of the obvious needs for some of these PRA activities for fuel cycle facilities.

59. On page 6-23, the authors conclude that at the azeotrope the 1:1 ratio of tributyl phosphate and water exists. This implies a knowledge of the ternary phase diagram that should be referenced.

We will look further into this comment. From the site visit, we had some preliminary indications that the applicant has knowledge of the ternary phase diagram but this needs to be confirmed.

60. On page 6-29 there is a wonderful result that HEPA plugging and operator error of commission dominate the TK3000 scenario. This is an example of the power of the method the authors are employing. It also highlights the inability to deal effectively with the errors of commission by operators and this inability may deserve mention.

Thanks, we could not have said it any better.

61. The authors have done some fairly heroic Monte Carlo analyses of the scenarios, but they only report final results. I should think that they would want to also show what estimated probabilities are most crucial to the conclusions that scenario probabilities are high or low. I should think they would be able to do this by simple regression analysis and it would not take the nearly 100, 000 calculations to get meaningful results.

We will highlight the major contributors to each of the scenarios analyzed as suggested by DP.

Chapter 7: Summary and Conclusions

62. My view is that the authors do not highlight their most significant accomplishment in the Summary. They elect instead to drive to a bottom line assessment of the probability of red oil events in the process facility. They get to these results only by accepting the applicants hypothesis for the chemistry of formation of red oil and the nature of red oil decomposition. They never critically examine this hypothesis or consider the ramifications of any alternatives. They do not consider radiolytic processes. They do not consider formation of organic peroxides or ozonides that will not smoothly decompose following Arrhenius kinetics. Their probability estimates are plagued by a very severe lack of data.

We acknowledge the limitations in our analysis listed by DP: (1) no consideration of the possible radiolytic dissociation of organic compounds and the formation of new reactive species, (2) no consideration of the formation of organic peroxides or ozonides (see Attachment, however, for a discussion of this), and (3) a severe lack of data in addressing estimates of probability of system and component failures. As indicated in the introductory response, the analysis was limited by time and resources.

63. I think the authors would be better off highlighting the capability they have developed to identify the crucial safety systems associated with the four most susceptible elements of the process stream. The pioneering application of probabilistic methods creates a framework that can be expanded to address a variety of uncertainties in the process safety. This is a significant accomplishment even predicated as it is on the applicant's hypotheses concerning the red oil threat. What it allows is examination of alternatives to see if these alternative hypotheses will still be detected, prevented or mitigated by the proposed safety systems. What happens if micelles form? Can density systems or sampling detect these micelles? The authors could also highlight the crucial probabilities for which better values would aid assessment. Are the most important probabilities those associated with equipment reliability or those associated with operator performance? Compared to these capabilities, the citation of dubious estimates of upset frequency is very sterile indeed.

As indicated in the introductory response, we did accept, by and large, the applicant's hypothesis regarding the threat of a red oil excursion. The PRA was done to assess the robustness of the applicant's strategy for dealing with the red oil issue. Additional discussion will be added as suggested on the relative impact of equipment and human reliability to red oil excursions.

64. This framework the authors have developed, albeit incompletely because resource limitations, can be used to assess the safety and vulnerabilities of the proposed system. It can also be used by NRC to design its strategy for monitoring licensee performance once a system is placed into operation. There are challenges associated with the framework - some are suggested above. But, this appears to be a framework with sufficient potential that it is worth addressing the challenges.

We thank DP for these comments.

Attachment 1

A Note on Chemical Reactions Not Considered in the BNL Study

W.A. Mukaddam, CCTI

Theoretically a large number of chemical reactions, most of them at or below the level of detection, are possible and indeed take place when two or more chemicals are in contact for any length of time. However what is relevant to us here is the impact of these reactions on the process safety. There are two possible effects on safety of reactions and reaction products: (1) unstable separation and (2) heat generation in the case of exothermic reactions.

We should note that the discussion below is regarding the reviewer's comment about the chemical reactions and reaction pathways not adequately considered in the report. We agree with Dr. Powers that radiolysis, as a class of reactions, need to be considered. This writer is not sufficiently familiar with radiolytic reactions to adequately judge their impact.

Reaction products, even in trace quantities, can unexpectedly cause emulsions to form which may make phase separation difficult. The BNL team and the applicant have considered this possibility. The second unanticipated result is heat generation. Heat generation of any significance, meaning that amount which may exceed normal heat removal, requires relatively rapid reaction of a significant amount of reactants, and therefore involves major components and reaction pathways studied extensively, in fact with a specific purpose to determine the amount of heat that is generated. Hyder (equation 2 in Chapter 3 of the BNL draft report) by calculating the maximum heat release by stoichiometrically balanced equation of the predominant chemicals present bounds the problem.¹

Trace amounts can also initiate other reactions that can cause emulsions or generate heat. However, as we do not address a specific reaction mechanism, this possibility can be lumped together in one of the two results we considered above and need not be considered as separate call of reactions.

TBP and a diluent, usually kerosene, that is much less pure than HPT used here, is used to purify fertilizer grade phosphoric acid by an extraction process that is similar in many respect to the process used here. Fertilizer grade phosphoric acid, depending on the source of rock used, can have a large diversity of ionic impurities. Build up of these impurities in the solvent phase tends to deteriorate the extraction column performance principally by making separation difficult, a condition which, if not controlled, can eventually cause emulsions. Typically, a small solvent bleed is treated with caustic to remove the products of hydrolysis as well as other reactions. In addition, a small portion of the solvent is continuously taken out of the system to avoid buildup of chemicals not effectively removed by caustic treatment. The MOX facility has a similar caustic treatment, however we do not know if there is provision to bleed a portion of the solvent or replace the total solvent inventory periodically. These two methods will avoid buildup of reaction products.

The reviewer refers to ozonolysis of perhaps HPT as a source of reactions not considered in the BNL report. Ozonolysis of oleic acid is referred to as an example. We believe that the possibility of reactions to any substantive extent involving Criegee intermediate types is not probable. Oleic acid is industrially cleaved by ozone to two C9 carboxylic acids, palermonic and azeleic acids. However, this reaction requires an oxidation catalyst (e.g., V_2O_5), high ozone

partial pressure and above ambient temperature (minimum 50° C). More importantly, the principal difference between oleic acid and HPT is that unlike HPT, which is completely saturated, oleic acid contains a double bond at the C9 position. Stearic acid which is identical to oleic acid, except that it is saturated, is not known to undergo similar cleavage. Therefore, we believe that the use of HPT with very low bromine number is a much better choice than say commercially available kerosene. In addition, we expect that bromine number of the solvent system will be monitored to ensure that reactive species are controlled.

There is one possible, though highly unlikely scenario that may exceed Hyder's heat release results. Say a series of low level endothermic reactions take place at various parts of the plant building up unknown chemicals. This is in essence equivalent to building potential energy in chemicals. These then oxidize to form water and CO₂. The heat generated in this unlikely scenario can be larger than what Hyder calculates.